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CONTENTS

PAGE

L. WRIGHT. The size of atmospheric nuclei: some deductions from measurements of the number of charged and uncharged nuclei at Kew observatory 675

E. R. CONSTABLE. The effect of an acoustically absorbent lining upon the sound-insulating value of a double partition 690

H. HOATHER. The density and coefficient of expansion of liquid gallium over a wide range of temperature 699

ORMAN CAMPBELL. The determination of absolute units 708

ILLIAM COCHRANE. The structure of some metallic deposits on a copper single crystal as determined by electron-diffraction 723

OFESSOR W. WILSON. The mass of a convected field and Einstein's mass-energy law . 736

C. JACKSON. The paramagnetism of the rare-earth sulphates at low temperatures . 741

HARLES FABRY. Vision in optical instruments 747

T. S. APPLEYARD. The phenomenon of spreading in the first positive bands of nitrogen 763

LIPSON and C. A. BEEVERS. An improved numerical method of two-dimensional Fourier synthesis for crystals 772

F. BATES and A. BAQI. The magnetic properties of chromium . . . 781

F. BATES and L. C. TAI. The magnetic properties of amalgams . . . 795

eviews of books 810

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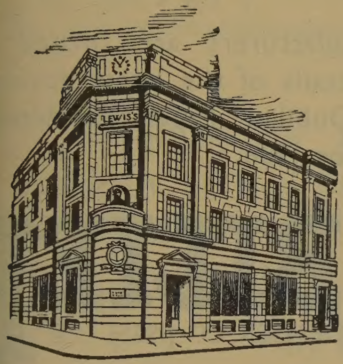

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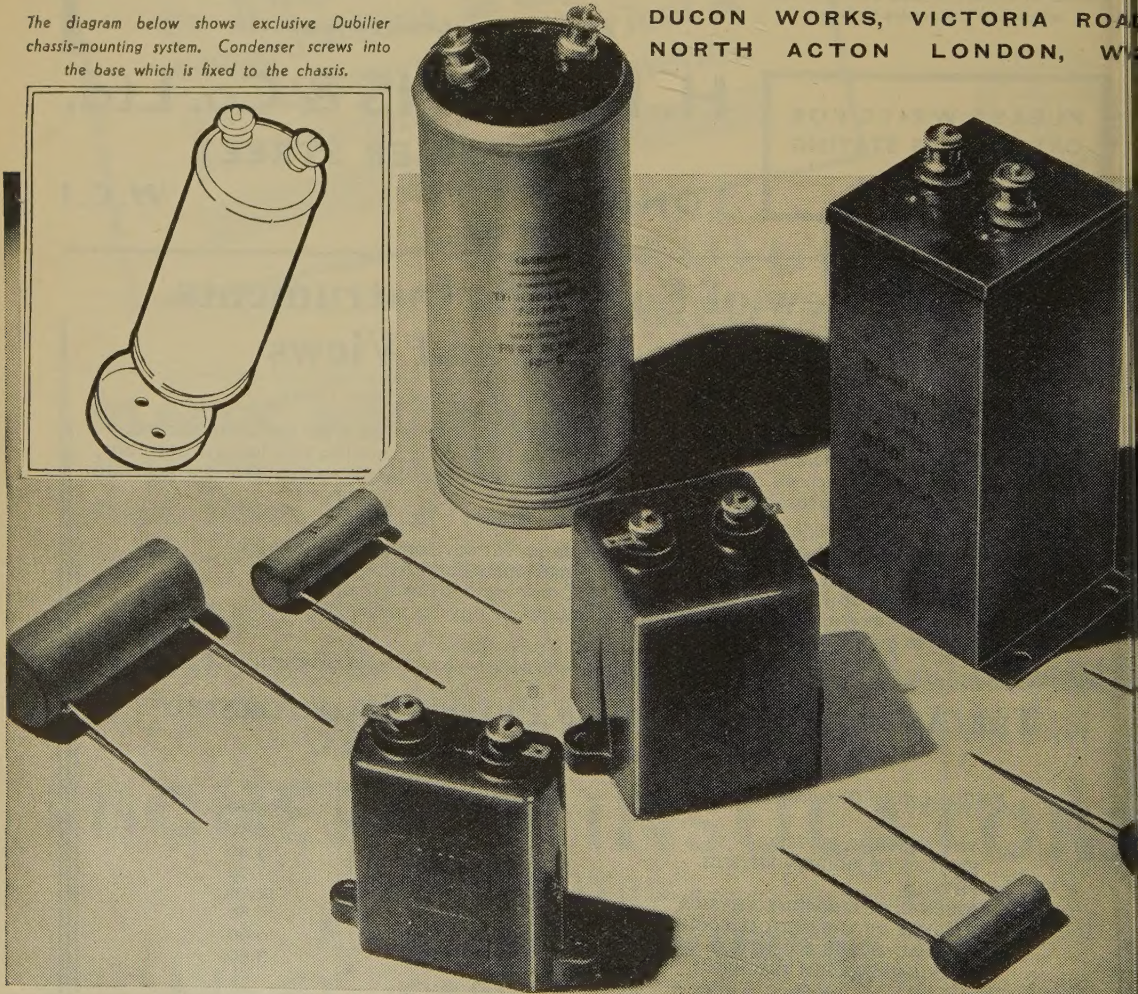

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THE SIZE OF ATMOSPHERIC NUCLEI: SOME DEDUCTIONS FROM MEASUREMENTS OF THE NUMBER OF CHARGED AND UNCHARGED NUCLEI AT KEW OBSERVATORY

BY H. L. WRIGHT, M.A.

Received January 23, 1936. *Read in title April* 4, 1936

ABSTRACT. The first object of this paper is to set out formulae to be used in determining the size of condensation nuclei from observation of the concentration in the atmosphere of charged and uncharged nuclei and observation of the numbers of small ions of either sign. It is well known that ratios of the combination coefficients which specify the rates of combination of small ions with charged or uncharged nuclei can be deduced from such observations. In the present analysis the following additional principles are assumed. (1) The combination coefficients are related to w, the mobility of small ions by Whipple's hypothetical equation

$$\eta_{12} - \eta_{10} = 4\pi e w,$$

and (2) combination between small ions and uncharged nuclei are produced solely by collisions due to the random Brownian movements of the small ions.

On the assumption that a small ion is equal in mass to eleven molecules of water it is deduced from Scrase's observations at Kew Observatory that so long as the relative humidity is less than 80 per cent the radius of a nucleus is approximately 3×10^{-6} cm. With higher humidities the radii are larger, at 82 per cent $4{\cdot}2 \times 10^{-6}$ cm. and at 89 per cent $4{\cdot}5 \times 10^{-6}$ cm. In the last section of the paper Köhler's theory of the growth of nuclei in an atmosphere in which humidity increases is applied, and on the assumption that the hygroscopic nuclei at Kew are of diluted sulphuric acid, it is found that in summer the mass of the acid in a nucleus is about 18×10^{-17} g., the corresponding mass in winter being 12×10^{-17} g. If the predominant nuclei are of common salt or of nitrous acid these estimates must be halved to give the mass of salt or of the latter acid in a nucleus.

§ 1. INTRODUCTION

LITTLE is known in detail of the size of the hygroscopic nuclei found in the air or of the changes in size which they undergo with varying conditions of humidity. It is fairly evident that as the air becomes damper the nuclei will grow larger, and, as Köhler has shown(1), some idea of the form of the variation in their size with relative humidity may be obtained from thermodynamical considerations.

N_0, N

It is also evident on general grounds that the small ions in the air, which move with high velocities, are more likely to collide with a large nucleus than with a small one, and so the frequency of recombinations between small ions and nuclei is another indication of the size of the nuclei. The frequency of recombinations cannot however be measured directly but has to be inferred from measurements of other quantities. Whipple's theory(2) of recombination coefficients provides a very simple method of inferring the frequency of recombinations as it leads to a relation between the recombination coefficients and a quantity which is easily measured, viz., the ratio N_0/N, where N_0 denotes the concentration of uncharged nuclei and N denotes the concentration of charged nuclei of one sign.

The publication, in a recent paper by Scrase(3), of a curve showing how the ratio N_0/N at Kew Observatory varies with the relative humidity presents an opportunity of co-ordinating these two lines of approach to the problem of determining the size of nuclei. Values of the radius of the nuclei may be derived from those of N_0/N, and the curve given by Scrase may be used to determine the association between the radius of the nuclei and the relative humidity at Kew. This association may then be compared with that which is to be expected on thermodynamical grounds. This in brief is the aim of the present paper.

Whipple's theory, on which the derivation of the recombination coefficients from the ratio N_0/N is based, is expressed mathematically by the following equations:

$$\eta_{12} - \eta_{10} = 4\pi e w_1, \quad \eta_{21} - \eta_{20} = 4\pi e w_2 \qquad \ldots\ldots(1\cdot1),$$

w_1, w_2
η_{12}, η_{21}
η_{10}, η_{20}
e

where w_1, w_2 denote the mobilities of the positive and negative small ions respectively, η_{12}, η_{21} denote the recombination coefficients between small ions and oppositely charged nuclei, η_{10}, η_{20} denote the recombination coefficients between small ions and uncharged nuclei, and e denotes the elementary electric charge.

Values of the radius of the nuclei may be derived from those of η_{10} by use of the following formula:

$$\eta_{10} = \pi r^2 U \qquad \ldots\ldots(1\cdot2),$$

r, U

where r is the radius of the nuclei, and U is the average value of the Brownian velocity of small ions due to thermal agitation. This formula, which may conveniently be called the Brownian hypothesis, is obtained from considerations of the Brownian movement of the small ions as set forth in § 4 below.

In a paper(4) published in the *Philosophical Magazine* in July 1934, Dr Harper obtained formulae expressing η_{12} and η_{10} in terms of the radius of the nuclei and the mean free path of the small ions. Harper has subsequently corrected(5) his formulae for a numerical error which occurred in his previous work, but he informs me that he is not satisfied with the mathematical approximations which he used and that he is now recalculating η_{10} by exact methods. Pending publication of the new formulae it has been thought better to make no use of Harper's original formulae in the present paper. Accordingly our calculations will be based on Whipple's assumption and the Brownian hypothesis.

§ 2. THE RADIUS OF THE NUCLEI AS DEDUCED FROM THE KEW OBSERVATIONS

The diagram given by Scrase, showing the variation in the total concentration Z of nuclei and in the ratio N_0/N with relative humidity, is reproduced in figure 1, Z and the values corresponding to the points in the diagram are tabulated in table 1. Each value is derived from the mean of between 10 and 12 individual observations of Z and N_0 with the Aitken nucleus counter, N being defined by the equation

$$Z=N_0+2N.$$

§ 3. VALUES OF η_{10}

The first step in evaluating the radius of the nuclei is to calculate the values of the recombination coefficient η_{10}. These may be found from the formula

$$\eta_{10}=4\pi e w_1 \frac{1+fN_0/N}{(N_0/N)^2-1} \qquad \ldots\ldots(3\cdot1),$$

where $f=n_2w_2/n_1w_1$, n_1 and n_2 denoting the concentration of positive and negative f, n_1, n_2 small ions respectively.

This formula follows immediately from (*a*) the equilibrium equations for nuclei, viz.,

$$\eta_{10}n_1N_0-\eta_{21}n_2N_1=0=\eta_{20}n_2N_0-\eta_{12}n_1N_2,$$

where N_1 and N_2 denote the concentration of positive and negative large ions N_1, N_2 respectively, (*b*) Whipple's formulae (1·1), viz.,

$$\eta_{12}-\eta_{10}=4\pi e w_1, \quad \eta_{21}-\eta_{20}=4\pi e w_2,$$

and (*c*) the assumption that

$$N_1=N_2=N,$$

which is justified in the present instance by the fact that at Kew the space charge is always found to be small. From observations of the potential-gradient at various heights Scrase has shown(6) that on the average the space charge at Kew corresponds almost exactly to the excess of positive small ions, about 60 per cm.³ In still air, when the small-ion content is low, the space charge is rather larger and corresponds to an excess of about 300 positive ions per cm.³; even if this were entirely due to large ions, the concentration of which in quiet conditions at Kew is about 30,000 per cm.³, the ratio N_1/N_2 would only be 1·02. Hence, except possibly when individual cases are under consideration, the assumption that N_1 and N_2 are equal at Kew is not likely to lead to serious error.

In an earlier paper(7), in which I obtained a formula relating N_0/N to the radius of the nuclei, it was assumed that there was equality between the frequencies with which small ions of either sign combine with uncharged nuclei. It may be shown that this is equivalent to assuming that the value of f, or n_2w_2/n_1w_1, is unity. Such an assumption is not supported by observations at Kew, where although the mobilities w_1 and w_2 remain fairly constant, equal to 0·98 and 1·05 cm./sec. per V./cm. respectively, the ratio n_2/n_1 on the other hand is subject to a systematic variation with nucleus content, decreasing from 0·76 when the concentration of nuclei is 11·8 per mm.³ to 0·65 when the concentration is 62·4 per mm.³ There are indications that with higher concentrations of nuclei, that is when the values of n_1 and n_2 are

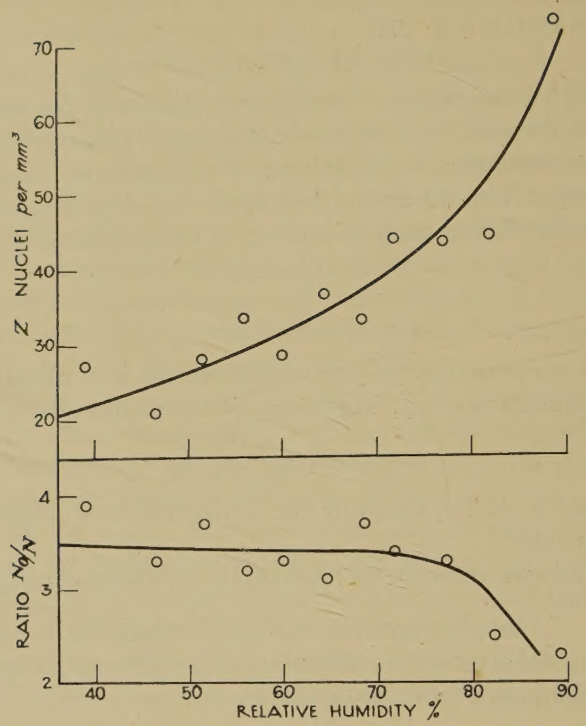

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Figure 1. Variation in nucleus-content and in the ratio N_0/N with relative humidity. (Kew Observatory. 15 h. G.M.T.)

Table 1. Variation in nucleus-content and in the ratio N_0/N with relative humidity at Kew, and deduced values of the recombination coefficient η_{10} and the radius of the nuclei

Relative humidity (per cent)	39	46·5	51·5	56·1	60·1	64·6
Concentration of nuclei per mm³	27·1	21·0	28·2	33·5	28·5	36·7
Ratio N_0/N	3·9	3·3	3·7	3·1	3·3	3·1
Recombination coefficient η_{10} deduced from Whipple's formulae (10^{-6} cm³/sec.)	0·49	0·61	0·52	0·66	0·63	0·68
Radius of nuclei r deduced from Brownian hypothesis (cm. × 10^{-6})	3·0	3·3	3·1	3·5	3·4	3·5
Values of Q deduced from thermodynamical equation (cm³ × 10^{-18})	17	22	15	19	17	17
	Mean 18					
Relative humidity (per cent)	68·6	71·8	77·2	82·2	89·2	
Concentration of nuclei per mm³	33·1	44·0	43·6	44·3	72·3	
Ratio N_0/N	3·6	3·4	3·3	2·5	2·3	
Recombination coefficient η_{10} deduced from Whipple's formulae (10^{-6} cm³/sec.)	0·53	0·59	0·62	0·97	1·09	
Radius of nuclei r deduced from Brownian hypothesis (cm. × 10^{-6})	3·1	3·3	3·4	4·2	4·5	
Values of Q deduced from thermodynamical equation (cm³ × 10^{-18})	11	10	10	15	12	
	Mean 12					

small, the value of n_2/n_1 may be still lower, but in these circumstances observations of n_1 and n_2 are not very reliable.

As however the value of η_{10} deduced from equation (3·1) is not highly sensitive to changes in the value of n_2/n_1, an inaccuracy of 0·06 in n_2/n_1 leading to an error of only 6 per cent in η_{10}, we may here adopt an average value of n_2/n_1 equal to 0·70 without introducing serious error. We shall therefore take

$$f = 0{\cdot}70 \times 1{\cdot}05/0{\cdot}98 = 0{\cdot}75.$$

The values of η_{10} obtained from those of N_0/N by use of the formula (3·1) are shown in table 1. The scatter in these values, which is due to the scatter in the values of N_0/N, might have been avoided by utilizing smoothed values of N_0/N read from the curve in figure 1, but it was considered that the use of values of N_0/N derived from actual observations was preferable to working with hypothetical values obtained from a curve which it is not yet possible to locate with precision.

The values of η_{10} shown in the table are of the same order of magnitude as those deduced by Scrase from formula (3·1) with exact values of the coefficient f, and discussed by him in his paper; the point to which attention may be drawn here is the apparent absence of systematic variation until humidities of about 80 per cent are reached.

§ 4. THE BROWNIAN HYPOTHESIS

Values of the radius of the nuclei may be deduced from those of η_{10} by use of the Brownian hypothesis (1·2) which may be formulated as follows. According to the simple view of the recombination coefficient between small ions and uncharged nuclei, forces due to electrical attraction may be ignored and only random collisions due to thermal agitation need be considered. The nuclei, being very large and inert compared with the small ions, may be regarded as stationary targets which the small ions approach normally from all directions with a velocity equal to the radial component of their Brownian velocity. Divergence of the small ions from the normal path owing to attraction by small ions of opposite sign may be neglected when nuclei are numerous, since in these circumstances the frequency of recombination with small ions of opposite sign is negligible compared with the frequency of recombination with nuclei.

If the ions and the nuclei were merely geometrical points we could say that the number of small ions crossing the boundary of a sphere of radius R in time t is equal to $4\pi R^2 n_1 v t$, where v is the average radial component of their velocity. Of these half enter and half leave the sphere, so the number entering the sphere is $2\pi R^2 n_1 v t$. Of these a certain proportion have been inside the sphere previously, but if R is not large compared with the mean free path that proportion must be small. *We make the assumption that the proportion is negligible when R is put equal to r, the radius of an uncharged nucleus* and deduce that the probable number of ions colliding with the nucleus in time t is $2\pi r^2 n_1 v t$. Further, since the average value of the cosine of the angle which the line of approach makes with the radius of nucleus is $\frac{1}{2}$, we have $v = \frac{1}{2}U$, where U is the mean velocity of the ions. Hence the number of collisions in unit volume and in unit time is $\pi r^2 n_1 U N_0$.

The frequency of recombination is by definition $\eta_{10}n_1N_0$. Hence if each collision is followed by recombination we have

$$\eta_{10}=\pi r^2U \qquad \text{......(1·2).}$$

It may be noticed that this is a limiting case of Harper's formula for η_{10}.

Formula (1·2) is different from that given in my earlier paper(7), referred to above. In deriving the earlier formula, which is erroneous, the fact was overlooked that the number of small ions colliding with an uncharged nucleus is only one-half of the number crossing the boundary of a sphere equal in size to the nucleus. Moreover, the value of v was taken to be the root of mean square of the radial component instead of the average value. According to the new formula the values of the radius of the nuclei given in my earlier paper would be increased by about 50 per cent.

§ 5. THE VALUE OF U

If the distribution of velocity amongst the small ions is Maxwellian then

$$U=\sqrt{\frac{8}{3\pi}}.C \qquad \text{......(5·1),}$$

C where C is the root of mean square or standard velocity. If a small ion consists of
n' a cluster of n' molecules of water vapour, each of mass m, then

$$\tfrac{1}{2}n'mC^2=3R\theta/2N' \qquad \text{......(5·2),}$$

R, θ where R is the gas constant, $8·32\times 10^7$ ergs per gram-molecule, θ is the absolute
N' temperature (say 283 degrees in the present case), and N' is Avogadro's number. Accordingly

$$U^2=\frac{8}{\pi}\frac{R\theta}{N'n'm} \qquad \text{......(5·3).}$$

Remembering that the mass of one molecule of water vapour is $18/N'$ we find that

$$U=10^4\times\sqrt{\frac{33}{n'}} \qquad \text{......(5·4).}$$

It is usually considered(8, 9) that the number of molecules* in a small ion cluster is about 10 or 12. Taking $n'=11$, we have

$$U=1·73\times 10^4 \text{ cm./sec.} \qquad \text{......(5·5).}$$

---

* Loeb, discussing the cluster theory of the formation of small ions(9) shows that a monomolecular layer cluster would be stable. He goes on to say, "Were the nucleus and molecules spheres of the same size the maximum number of molecules in a stable cluster would be 12. A cluster of more than 12 molecules would require another layer, for 12 molecules is all that can be placed round a sphere of the same size". He then shows that if there were another layer of molecules the cluster would be unstable, for the kinetic energy of agitation would be greater than the potential energy, and so the molecules would not be bound in a closed orbit. Finally "it is very unlikely that the ion cluster numbers more than 12 molecules".

§ 6. THE VALUES OF r

With this value of U the formula (1·2) becomes

$$\eta_{10} = 5{\cdot}45 \times 10^4 r^2 \qquad \text{......(6·1).}$$

Values of r deduced from those of η_{10} by means of equation (6·1) are shown in table 1 and are plotted in figure 2 against the values of the relative humidity with which they are associated. It will be observed that the changes in r are but slight until the relative humidity attains a value equal to about 80 per cent, conforming with the statement frequently made that condensation on nuclei commences when the relative humidity reaches about 80 per cent. Since it is evident on physical grounds that condensation will commence whenever there is an increase in relative humidity, it would be more strictly correct to say that the effect of condensation begins to be appreciable when the relative humidity reaches about 80 per cent.

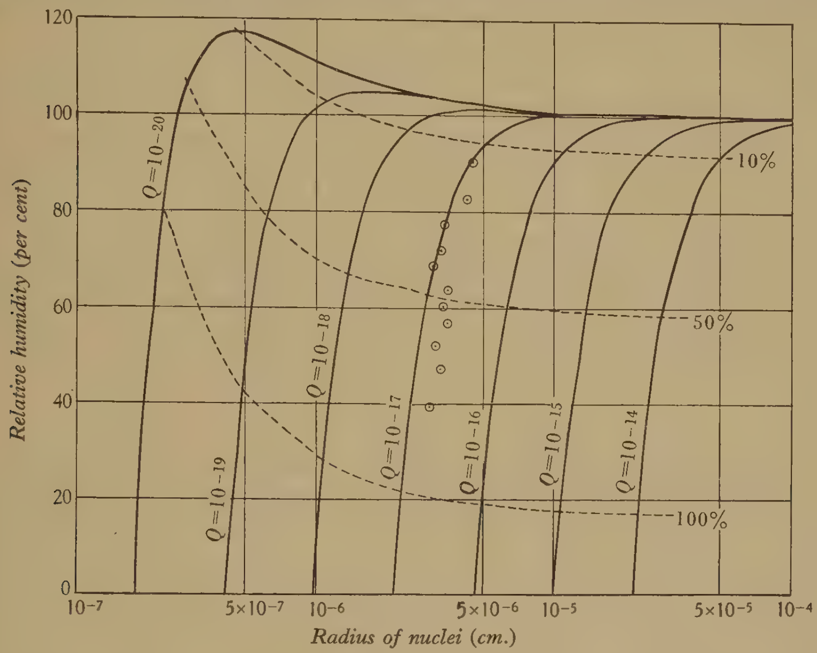

Figure 2. Variation in the radius of nuclei with relative humidity. The full lines represent the equation $H/100 = \exp\{P/r\} - Qr^3$ for $P = 11{\cdot}8 \times 10^{-8}$ and various values of Q. The broken lines represent the equation $c/100 = 1{\cdot}2\ Q/r^3$. ⊙ denotes values at Kew Observatory at 15h.

The form of the variation in r with relative humidity, as shown by the plotted points, approximates closely to that of the family of curves drawn in the diagram. These curves may be obtained from theoretical considerations as will be shown below.

§ 7. COMPARISON WITH VALUES OBTAINED BY OTHER METHODS

The values which we have obtained for the radius of the nuclei are of the same order of magnitude as that given by Thomson(10) for the radius of the large ion, generally supposed to be identical with a charged nucleus. From considerations of the motion of an electrified sphere through a viscous gas, by a method due to Cunningham⁽¹¹⁾, Thomson gives the following formula relating the mobility

K, r K of the large ion to its radius r

$$K=\frac{e\,(1+3l/2r)}{6\pi\mu r},$$

μ, l where μ is the coefficient of viscosity of the gas ($1{\cdot}83\times10^{-4}$ for air) and l is the length of the mean free path of a molecule of the gas (10^{-5} cm. for air).

There is some doubt as to the value of the coefficient of l/r to be used in this formula. Experimental work indicates that the factor 3/2 should be replaced by 0·864 according to measurements by Millikan⁽¹²⁾, and by unity according to those by McKeehan⁽¹³⁾. Thomson uses McKeehan's value of unity for the coefficient of l/r, and substituting for K the value of the mobility of Langevin ions, viz., 1/3000 cm./sec. per V./cm., finds r equal to $4{\cdot}5\times10^{-6}$ cm.

It may be noted that the most recent estimate of the radius of nuclei, deduced by Nolan and Guerrini⁽¹⁴⁾ from experimental determinations of the diffusion coefficients of the nuclei present in Dublin air, is $2{\cdot}85\times10^{-6}$ cm.

§ 8. VARIATION IN THE SIZE OF NUCLEI WITH RELATIVE HUMIDITY AS DEDUCED FROM THERMODYNAMICAL CONSIDERATIONS

It is generally supposed that condensation nuclei, which are of ultra-microscopic dimensions in dry air and only become visible in saturated air in the form of fog, cloud, or rain, are formed by the condensation of water vapour on suitable hygroscopic substances when these happen to be produced in the air. One possible mechanism for the production of hygroscopic substances in air is the distintegration of sea spray by the action of wind on the surface of the sea; in this case the hygroscopic substance in the resulting nuclei would be one or more of the hygroscopic salts contained in sea-water. Another possible mechanism is indicated by some recent experiments by J. H. Coste and the present writer⁽¹⁵⁾ which were made in order to examine the constitution of the nuclei formed in the process of combustion, as it has long been known that copious formation of nuclei follows the combustion of any kind of fuel. These experiments suggest that the nuclei so produced are solutions of nitrous acid formed by the union of atmospheric oxygen and nitrogen at the high temperatures occurring in the neighbourhood of the flame, and their subsequent combination with water vapour. Nitrous acid is however unstable and it is probable that collisions between nitrous acid nuclei and molecules of sulphur dioxide gas, evolved when fuel is burned, result in the oxidation of the sulphur dioxide by nitrous acid to form trioxide, with the liberation of gaseous nitrous acid or oxides of nitrogen, the trioxide uniting with water to form sulphuric acid. Hence of the nuclei produced by combustion some may be nitrous acid and some sulphuric acid.

The newly formed hygroscopic droplets abstract molecules of water from the air until an equilibrium state is reached in which the pressure of water vapour at the surface of the droplet is equal to that of the vapour of the air. Any subsequent disturbance of the equilibrium state by an external influence, such as a change in temperature due to radiation, convection, or conduction, leads to inequality between the two vapour pressures and inaugurates a process either of condensation or of evaporation whereby molecules of water are exchanged between the droplet and the air until another stable state is reached.

Thus the equilibrium size of a droplet depends upon the amount of water vapour in the air, and the condition for equilibrium is equality between the vapour pressure at the surface of the droplet and that of the water vapour in the air. This condition may be expressed mathematically as follows.

§ 9. THE HUMIDITY EQUATION

The vapour pressure over the surface of a spherical droplet is greater than that over a plane surface owing to the effect of surface tension. It has been shown by Kelvin(16) that if p denotes the vapour pressure over a plane surface of water and p' that over a spherical droplet at the same temperature

p, p'

$$\frac{p'}{p} = \exp \frac{2T}{\sigma R \theta r} \qquad \text{......(9·1)},$$

where T denotes the surface tension, σ the density of the liquid, R the gas constant for the vapour, θ the temperature of the droplet, and r the radius of the droplet.

T, σ, R, θ, r

In the case of a solution, however, the vapour pressure at the surface is less than that over pure water by an amount δp, where

$$\frac{\delta p}{p} = CM \qquad \text{......(9·2)},$$

M denoting the number of gram-molecules of solute per 1000 g. of solution and C a quantity which depends on the nature of the solute and for a given solute varies slightly with the concentration. Values of C for a great many substances are to be found in the *International Critical Tables*, **3**, 292. Average values of C for those substances of which atmospheric nuclei seem most likely to be constituted are shown in table 2. The hygroscopic properties of nitrous acid are not known owing to its instability, but as it is very attractive to water, its hygroscopic properties may be supposed to be not greatly different from those of sulphuric acid. Accordingly the value of C for sulphuric acid may also be used provisionally for nitrous acid.

M, C

Table 2. Molecular weights and hygroscopic factors for various substances

Chemical formula	$MgCl_2$	$NaCl$	HNO_2	H_2SO_4
Molecular weight w	95	58	47	98
Hygroscopic factor C	8×10^{-2}	4×10^{-2}	(4×10^{-2})	4×10^{-2}
m/Q or $\pi \sigma w/750\,C$	5	6	(5)	10

The quantity M is a function of the radius of the droplet since it depends on the concentration of the solution. If m denotes the mass of the solute contained

m

w in the nucleus, which for a given nucleus remains constant, and w denotes the molecular weight of the solute, then the mass of the solution being $\frac{4}{3}\pi r^3\sigma$, we have

$$M = 1000\,\frac{m/w}{\frac{4}{3}\pi r^3\sigma} = \frac{750m}{\pi r^3\sigma w}$$

and so equation (9·2) becomes

$$\frac{\delta p}{p} = \frac{750\,mC}{\pi r^3\sigma w} \qquad \text{......(9·3)}.$$

Combining* equations (9·1) and (9·3) we have for the vapour pressure p' at the surface of a hygroscopic droplet

$$\frac{p'}{p} = \exp\left\{\frac{2T}{\sigma R\theta r}\right\} - \frac{750\,mC}{\pi r^3\sigma w} \qquad \text{......(9·4)}.$$

e' If e' denotes the pressure of water vapour in the surrounding air, the condition for equilibrium is that

$$p' = e' \qquad \text{......(9·5)}.$$

Assuming that the temperature of the droplet is the same as that of the surrounding air, p is equal to the vapour pressure over a plane surface of water at *air* temperature, and hence if H denotes the relative humidity, we have from the definition of relative humidity

H

$$\frac{H}{100} = \frac{e'}{p} \qquad \text{......(9·6)}.$$

Equations (9·4), (9·5) and (9·6) give at once

$$\frac{H}{100} = \exp\left\{\frac{2T}{\sigma R\theta r}\right\} - \frac{750\,mC}{\pi r^3\sigma w},$$

which it is convenient to write in the form

P, Q

$$\frac{H}{100} = \exp\frac{P}{r} - \frac{Q}{r^3} \qquad \text{......(9·7)},$$

where $P = \dfrac{2T}{\sigma R\theta}$ and $Q = \dfrac{750\,mC}{\pi\sigma w}$.

This is the desired equation expressing the equilibrium condition between droplets and aqueous vapour, and when the values of P and Q are known the equation can be used to find the radius of nuclei in equilibrium with air of given relative humidity.

§ 10. GRAPHICAL REPRESENTATION

Since T, σ and R vary but slightly, the quantity P depends chiefly upon the temperature θ of the droplets. The temperature of droplets in the free air near the earth's surface may be subject to a diurnal variation of some 30° C., a variation of about 5 per cent from the mean, but by partial differentiation of equation (9·7) it is found that the error in the value of H due to an error of as much as 10 per cent in P is only 2 per cent for very small droplets of radius 6×10^{-7} cm., and 1 per cent for droplets of radius 10^{-6} cm., and decreases rapidly for larger droplets. Thus relatively small changes in the temperature of nuclei such as those due to diurnal variation may be neglected, and an average value of P may be adopted. Taking $T=74$ dyne/cm.^{2}, $\sigma=1$ g./cm.^{3}, $R=(83{\cdot}15\times10^6/18)$ ergs, and $\theta=283°$ K., the value of P is found to be $11{\cdot}3\times10^{-8}$. This value will be used throughout.

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* It should be remarked that, as Bennett(17) has pointed out, it is open to question whether equation (9·2) is applicable to the case of small surfaces.

The quantity Q depends chiefly upon the mass of hygroscopic substance, when the nature of the substance is determined, that is, when w and C are known. The hygroscopic factor C may vary with the concentration of solution, particularly when the solution becomes very dilute and the phenomenon of dissociation occurs. As shown by the values of m/Q in table 2, which are calculated from those of w and C, the value of Q is roughly equal to one-fifth that of the mass of hygroscopic substance in the nucleus, except in the case of sulphuric-acid nuclei for which the value of Q is one-tenth that of m.

Since nothing is known as to the value of m we must consider Q as liable to extensive variation. By assigning in turn different values to Q, the variation of r with H given by equation (9·7) may be plotted in the form of an isopleth diagram. Figure 2 is such a diagram, the different values adopted for Q being 10^{-20}, $10^{-19}\ldots10^{-14}$. Semi-logarithmic scales are used in the figure owing to the wide range in the values of r which have to be taken into account.

§ 11. THE CONCENTRATION OF SOLUTE IN THE NUCLEI

A rough estimate may be formed of the concentration of solute in the nuclei. If the concentration is c per cent we have, since the mass of the droplet is $\frac{4}{3}\pi r^3\sigma$,

$$\frac{c}{100}=\frac{m}{\frac{4}{3}\pi r^3\sigma}\simeq\frac{5Q}{\frac{4}{3}\pi r^3\sigma}=1{\cdot}2\,\frac{Q}{r^3}\qquad\ldots\ldots(11{\cdot}1),$$

except for sulphuric acid for which the coefficient of Q has to be doubled. Isopleths of concentration equal to 10, 50 and 100 per cent have been constructed to represent this approximate formula and are shown by the broken lines in figure 2. For sulphuric-acid nuclei the values would be double those marked in the diagram, which apply to the other substances. It should be emphasized that the values of the concentration are only rough approximations and are intended to serve merely as a guide. No rigour can be claimed for inferences deduced from their use, and it is for this reason that the full curves in figure 2 have been continued beyond the broken curve denoting 100-per-cent concentration.

It may be noted here that the use of unity for the density of nuclei is strictly justified only when the concentration of solute is not excessive. The changes in the form of the isopleths due to changes in density are however slight and are not worth considering at this stage.

§ 12. THE CASE OF CHARGED NUCLEI

It will be remarked that we have not considered the influence on the size of the nuclei exerted by the alternating acquisition and loss of electric charge which they experience. The potential energy due to the presence of an electric charge on a droplet reduces the vapour pressure at the surface, but it is readily seen that for droplets of nuclear dimensions this effect is ordinarily negligible.

As has been shown by Thomson$^{(18)}$, the effect of electric charge may be represented by the addition of a term in equation (9·1) which becomes

$$\frac{p}{p'}=\exp\frac{1}{\sigma R\theta}\left\{\frac{2T}{r}-\frac{n^2e^2}{8\pi r^2}\right\},$$

n, e where n denotes the number of elementary charges e carried by the nucleus. The ratio of the two terms within the brackets is, when the values of e and T are substituted, $61\times10^{-18}\,n^2/r^3$, and is less than 1 per cent in the case of singly charged nuclei ($n=1$) if $r>2\times10^{-7}$ cm., and in the case of doubly charged nuclei ($n=2$) if $r>3\times10^{-7}$ cm. The values found for the radius of the nuclei at Kew are considerably higher than these, and unless the nuclei are multiply charged the difference between the sizes of the charged and uncharged nuclei is negligibly small.

Multiply charged nuclei are rare, and although Scrase$^{(19)}$ has found that droplets in fog carry charges of $34e$ the radius of fog droplets is so large that the effect of even such a high charge is in these circumstances insignificant. It would appear then that the effect of electric charge on the equilibrium size of nuclei may normally be regarded as a second-order quantity, becoming appreciable only in the rare case of multiply charged intermediate ions.

§ 13. DISCUSSION OF THE ISOPLETH DIAGRAM

The curves drawn in figure 2 are essentially similar to those given by Köhler$^{(1)}$ showing how the vapour pressure at the surface of droplets, which contain known concentrations of salts, chiefly sodium chloride, and are at a temperature of 273°, varies with a quantity proportional to the logarithm of the volume of the droplet. The most remarkable feature of the family of curves is that each of them crosses the saturation line and then returns to it. This means that when supersaturation occurs, owing to the depression of the air-temperature below that of the dew point, water is deposited on the droplets which consequently increase in size and are eventually in equilibrium with air which is just saturated. Thus the presence of the nuclei prevents conditions of high supersaturation being attained and intensified. The final size of the droplets would appear to be determined by the number taking part in the process and by the depression of the temperature below the original dew-point temperature, since the presaturation size of the nuclei is usually negligible in comparison.

Another important phenomenon indicated by the curves is the restriction of the deposition of moisture under conditions of supersaturation to those nuclei for which Q is greatest. Less supersaturation is required for deposition to occur on these, indeed for large values of Q the supersaturation need only be trifling, and once the requisite degree of supersaturation is attained, the ensuing deposition of moisture upon nuclei in this group prevents the attainment of the higher supersaturation necessary for deposition to occur on the remaining nuclei. Bennett has remarked upon this, pointing out$^{(17)}$ that "the number of drops in a fog rarely attains a value as high as 1500 per c.c., while the number of Aitken nuclei is usually ten times this figure". Since in dry air the nuclei for which Q is greatest are those of greatest size and therefore those which on acquiring electric charges would be the slowest ions, it appears that, unless Q changes appreciably as saturation is approached, deposition of moisture when supersaturation is reached would occur most readily on the large ions of lowest mobility.

The curves indicate that in dry air the growth of nuclei with relative humidity is slow until humidities of about 80 per cent or so are reached, and agree very well with the form of the variation inferred from the Kew observations, as the plotted points show.

§ 14. THE VALUES OF m

It may be seen from the diagram in figure 2 that the plotted points may be divided into two categories, one in which the relative humidity is greater than 66 per cent, the other in which the humidity is less than this figure. Since at 15 h., when Scrase's observations were made, high humidities are associated with the winter months and low humidities with the summer months, this indicates an annual variation in the value of Q. From the values of Q shown in table 1, which are calculated from those of r and H by use of formula (9·7), it may be seen that the value of Q associated with low humidities, that is in summer, is on the average 18×10^{-18}, while that associated with high humidities, that is in winter, is 12×10^{-18}.

There are two sources of variation in Q, one being C, the hygroscopic factor, and the other m, the mass of hygroscopic substance in the nucleus. Generally, C may be expected to increase rather than decrease as the concentration of solution diminishes; whereas inspection of the isopleths of concentration in figure 2 shows that the category of points for which the concentration is least (the higher humidities) corresponds with the lower value of Q. Thus it appears that the source of variation in Q is to be found in variations in m, and the calculations imply that the value of m is less in winter than in summer.

If the nuclei consist of a substance for which the value of m/Q is 5, as we have assumed for nitrous acid (see table 2), the mass of hygroscopic substance in each nucleus corresponding to the above values of Q is 90×10^{-18} g. in summer and 60×10^{-18} g. in winter. Since the average values of the concentration of nuclei at Kew at 15 h. are(20) 20,000 per cm^3 in summer and 38,000 per cm^3 in winter it follows that the total concentration of hygroscopic substance in the nuclei in 1 cm^3 of air is 18×10^{-13} g. in summer and 23×10^{-13} g. in winter. If the nuclei consist of sulphuric acid, these values must be doubled (see table 2).

The conclusion that there is a greater concentration of hygroscopic substance present in winter than in summer seems reasonable in view of the increased combustion in winter and also of the relative absence of the convection which tends to expel atmospheric pollution from the lower atmosphere.

The value of the concentration of sulphuric acid in nucleus form, viz., about

4×10^{-12} g. per cm.^{3}, may be compared with the concentration of sulphuric acid in London air found, in the course of work not yet published, by Coste and Courtier, who analysed the condensate obtained by cooling air, freed from acid gases, by passing it through a vessel surrounded with ice. The amounts of sulphuric acid found by them varied from 4 to 20×10^{-12} g. per cm.^{3}, the higher results being usually associated with fog and the lower ones with rain.

Similar figures for nitrous acid may be obtained from the determination, by Francis and Parsons(21), of the oxides of nitrogen in the air of St James's Square, London. They found from 0·3 to 16·8 parts per 100 million by volume, calculated as nitric oxide, equivalent to from 6 to 354×10^{-12} g. per cm.^{3} of nitrous acid.

It will be noticed that these values are considerably in excess of the values deduced for Kew. This may be because the experimental values were obtained in air in the centre of London while Kew is near the outskirts, some ten miles from the centre. In the case of the oxides of nitrogen a large proportion of these are in gaseous form, and as the experimental results refer to the total concentration, gaseous and liquid, the amount of nitrous acid existing in liquid form as condensation nuclei must be much less than the total concentration found from the experiments.

§ 15. CONCLUSION

It should be pointed out that our treatment of the Kew observations does not take into account the possibility of the nuclei being heterogeneous. Thus the results should be considered as the average for various types of nuclei, if these in fact exist at Kew. It seems likely however that at Kew, fire-produced nuclei form a highly predominating group, and if this is the case it is a legitimate approximation to treat the nuclei as belonging to a single group. Further work along these lines may be expected to show the degree of accuracy of the approximation.

It appears from the foregoing analysis that, since P is not appreciably variable, the value of Q is the factor which determines the size of nuclei under prescribed humidity conditions in non-saturated air. Determination of the values of Q at different places and at different times of year provides a subject for further research which can hardly fail to yield information on the difficult problem of the origin and nature of hygroscopic nuclei.

§ 16. ACKNOWLEDGMENTS

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THE EFFECT OF AN ACOUSTICALLY ABSORBENT LINING UPON THE SOUND-INSULATING VALUE OF A DOUBLE PARTITION

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ABSTRACT. A study is made of the effect of rendering the interior of double partitions acoustically absorbent. A formula is derived for the effect of the treatment and is confirmed by measurements made upon double partitions containing various amounts of absorbent. The measurements show that considerable increases in the sound-insulation of a double partition can be obtained by the judicious use of it. In particular, in the case of a double window, an increase of some 8 db. can be obtained by covering with absorbent the wall surfaces enclosed between the two panes of glass.

§ 1. INTRODUCTION

Measurements made at the National Physical Laboratory and elsewhere have shown that the average sound-insulating effect of a single partition, e.g. a sheet of glass or a brick wall, is determined almost entirely by its weight per square foot. Consequently, high sound-insulation is only obtainable by making such partitions heavy. In many partitions this is undesirable, for instance a glass window; in others it is impracticable, for instance the wall of an aeroplane cabin or a partition in a modern multi-storey building. In such cases recourse is had to multiple partitions, double windows, double aluminium panels and double building-block partitions respectively being used.

In an earlier paper(1) the author has shown that the sound-insulating value of a light air-spaced double partition, in which the sole coupling between the components is the air in the interspace, is dependent upon the thickness of the spacing. It is the purpose of the present paper to describe how the sound-insulating value of such a partition may be increased by suitably disposing acoustical absorbent material within it.

§ 2. THEORETICAL CONSIDERATIONS

The calculations given below do not pretend to be exact, but serve to show the mechanism by which the absorbent interior of a double partition affects its sound-insulating qualities. It will appear later, however, that the formula obtained gives results which are in reasonable agreement with experiment.

Figure 1 represents an air-spaced double partition situated between two acoustically dead rooms, so that sound returned to the partition from the side remote from the sound source need not be considered.* The fixing of the two sheets is taken to be such that the energy transferred from one sheet to the other *via* the edges can be neglected.

The sound-reduction factor of the partition will, of course, vary with the angle of incidence of the sound, but if the sound-reduction is first calculated for a ray having a particular angle of incidence, the result can be generalized for all angles of incidence by using mean values for the sound-reduction factors and absorption coefficients of the constituents of the partitions.

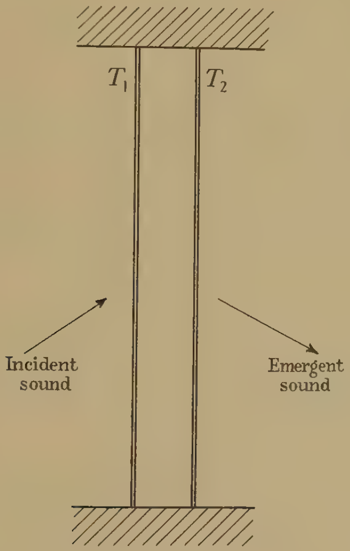

Figure 1.

Let the sound-reduction factors of the transmitting panels T_1 and T_2 be R_1 R_1
and R_2 respectively for the particular angles of incidence considered. R_2

If sound of energy dE, being part of a ray of sound travelling in the direction dE
of the arrow, falls upon the partition during time dt, it will be divided into two dt
parts by T_1—a transmitted part of energy dE/R_1 and a reflected part of energy $dE\,(1-1/R_1)$. The transmitted sound will be reflected backwards and forwards between the interior surfaces of the partition and some of the reflections will take place at the transmitting panels T_1 and T_2. At each incidence upon the two transmitting surfaces average fractions $1/R_1$ and $1/R_2$ respectively of the energy of the sound will be transmitted out of the partition. There will be a certain average circuit which the sound traverses between successive incidences upon T_2. In this circuit

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* This restriction, while simplifying the problem, does not render the conclusions less general, since the only effect of making the rooms reverberant would be to pass some sound back through the partition into the source room by an amount which can be allowed for by means of the ordinary theory of coupled rooms.

m

the sound visits the other surfaces and by absorption and transmission is reduced to a fraction $1/m$, say, of its value at the previous reflection.

Now such a ray may be considered as a stream of elements of energy such as the above. Let the ray have been incident upon the partition for a sufficient time for equilibrium to have become established. Then, assuming that sound passing through T_1 proceeds directly to T_2 and does not suffer a reflection at the margins on the way,* during any time interval dt there will be incident upon T_2 elements of energy which have travelled directly and others which have made one, two or more circuits. The former have energy dE/R_1, the others dE/mR_1, dE/m^2R_1 etc.

Thus the total energy falling upon T_2 in time dt due to the ray will be

$$\frac{dE}{R_1}\left(1+\frac{1}{m}+\frac{1}{m^2}+\text{etc.}\right)=\frac{mdE}{R_1\,(m-1)}.$$

Thus of the energy dE which is incident upon the partition, a fraction $mdE/\{R_1R_2\,(m-1)\}$ is transmitted through T_2. The reduction of sound by the partition as far as the particular ray we are considering is concerned is thus $R_1R_2\,(m-1)/m$.

Taking the average of all incident rays, the sound-reduction factor will be

$$\bar{R}_1\bar{R}_2\,(1-1/\bar{m}) \qquad \text{......(1)},$$

$\bar{R}_1$, $\bar{R}_2$
$\bar{m}$

where $\bar{R}_1$ and $\bar{R}_2$ are the sound-reduction factors of the two leaves T_1 and T_2 averaged over all angles, and $\bar{m}$ is the mean value of m for all such angles.

Thus the effect of changing the absorbent character of the interior of the partition is to change its sound-reduction by a factor

$$\frac{1-1/\bar{m}'}{1-1/\bar{m}''} \qquad \text{......(2)},$$

$\bar{m}'$, $\bar{m}''$

where $\bar{m}'$ and $\bar{m}''$ are the values appropriate to the two conditions.

We see from equation (1) that the reduction can never be greater than R_1R_2.

A word of caution is called for here, namely that R_1 and R_2 are the sound-reductions of T_1 and T_2 not when considered by themselves but when combined in the form of the double partition. This warning is necessary since, as shown in a previous paper$^{(1)}$, two sheets such as we are considering react upon each other through the elasticity of the separating air and acquire new resonant frequencies in addition to those they would possess by themselves. It thus happens that their effective sound-reduction may be lower when combined than when taken separately.

§ 3. CALCULATION OF $\bar{m}$

$A_1 \ldots A_6$
$\alpha_1 \ldots \alpha_6$

Let the areas of the transmitting faces T_1 and T_2 be A_1 and A_2 and the areas of the other four interior surfaces be A_3, A_4, A_5 and A_6. Let the absorption coefficients of the six surfaces be α_1, α_2, α_3, α_4, α_5, α_6, averaged over all angles of incidence.

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* In view of the usual proportions of this type of partition, this must be true of the greater part of the sound.

Then in any given time-interval the sound will be reflected at each of the surfaces a number of times proportional to its area. Thus for each reflection at T_2 (by which the sound leaves the partition) there will be A_1/A_2 reflections at T_1, A_3/A_2 reflections at surface (3), and so on:

At each reflection at T_1 the sound loses, by absorption and transmission, an average fraction $(\alpha_1 + 1/R_1)$, and a similar expression holds for T_2. At each reflection at the other surfaces, which are assumed not to transmit appreciably, it will lose fractions α_3, α_4, α_5 and α_6 respectively.

Thus in the complete circuit the sound is reduced on an average to a fraction $1/m$ such that

$$\frac{1}{m}=\left(1-\alpha_1-\frac{1}{\bar{R}_1}\right)^{A_1/A_2}\left(1-\alpha_2-\frac{1}{\bar{R}_2}\right)(1-\alpha_3)^{A_3/A_2}(1-\alpha_4)^{A_4/A_2}(1-\alpha_5)^{A_5/A_2}(1-\alpha_6)^{A_6/A_2} \quad \text{......(3)},$$

which is the result required.

It may be noted that this formula expresses what was implied in the method of derivation: provided that the areas are the same, the absorbent is equally effective whether placed on the leaves of the partition or on the side walls. If, as in the usual partition, the areas of the transmitting surfaces are equal to A, and the interior surfaces of the sides of the partition all have the same absorption coefficient α, equation (3) becomes

$$\frac{1}{m}=\left(1-\alpha_1-\frac{1}{\bar{R}_1}\right)\left(1-\alpha_2-\frac{1}{\bar{R}_2}\right)(1-\alpha)^{\frac{S}{A}} \quad \text{......(4)},$$

where $$s=A_3+A_4+A_5+A_6.$$

Thus, by combining equation (4) with equation (1), we have that the sound-reduction R due to such a partition will be given by

$$R=\bar{R}_1\bar{R}_2\left(1-\left[\left(1-\alpha_1-\frac{1}{\bar{R}_2}\right)\left(1-\alpha_2-\frac{1}{\bar{R}_2}\right)(1-\alpha)^{\frac{S}{A}}\right]\right) \quad \text{......(5)}.$$

When the absorption coefficients are small equation (5) takes the simple form

$$R=\frac{\bar{R}_1\bar{R}_2}{A_2}\times(\text{total absorbing power of the interspace}),$$

the total absorbing power including, of course, the losses due to transmission through the panels.

By taking logarithms of both sides of equation (3) we obtain

$$A_2\log_e\left(\frac{1}{m}\right)=A_1\log_e\left(1-\alpha_1-\frac{1}{\bar{R}_1}\right)+A_2\log_e\left(1-\alpha_2-\frac{1}{\bar{R}_2}\right)+\sum_3^6 A_r\log_e(1-\alpha_r).$$

The expression on the right bears an obvious resemblance to the denominator in G. Millington's formula for the reverberation period of a room⁽²⁾, viz.:

$$T=\frac{0\cdot05V}{-\Sigma A_1\log_e(1-\alpha_1)},$$

where T is the reverberation period and V the volume. This is a consequence of the use of Millington's method of calculating the effect of the absorbent.

§ 4. EXPERIMENTAL RESULTS

The above calculations show that the introduction of absorbent into the interior of a partition should, when the interior is initially reverberant, considerably increase its sound-insulation. To test this and to compare the amount of the increase with that predicted by equation (5), an air-spaced double partition 2 ft. 6 in. square was built.

Light aluminium sheets weighing 0·3 lb. per square foot were used, since experience had shown that coupling between the edges is small in this type of partition. In order that a wide range of absorption coefficients for the interior surfaces might be used, special care was taken to commence with a highly reverberant interior. For this purpose the partition was formed by fixing the two aluminium sheets in an aperture in a steel diaphragm 9 in. thick. The side walls of the partition were thus of heavy steel. The diaphragm was mounted in the test aperture between the large sound-transmission rooms at the National Physical Laboratory. Two separations of the sheets were experimented with, namely 8 in. and 4 in.

Arrangements were made for supporting sheets of absorbent material against the steel interior surfaces of the partition. This position was chosen because if the absorbent had been hung against the aluminium sheets their mass and hence their sound-reduction would have been affected. Two absorbents were tried in the 8-in. partition, one an acoustic felt with an absorption coefficient of about 0·6 and the other a fibre board with an absorption coefficient of about 0·2. The acoustic felt only was tried in the 4-in. partition.

Measurements of the sound-reduction factor of the double partition were made both with and without the absorbent in position. Measurements were also made of the sound-reduction factor of one of the sheets of aluminium alone. The measurement rooms were used in a reverberant condition so that sound was incident at all angles upon the partition, and to minimize stationary wave effects, a warble test note was used, the note varying periodically in frequency by 10 per cent of its mean value. The following were the mean frequencies used for the measurements: 200, 400, 800, 1000 and 2000 cycles per second.

In each case an increase in the sound insulation was observed when the interior of the partition was rendered absorbent. The results obtained are given in table 1 below, in which are also given, for comparison, the values calculated from equations (2) and (3). It will be seen that the agreement is fairly good.

For the calculated values it is necessary to assume some value for the absorption coefficients of the aluminium and steel surfaces. A reasonable estimate can be formed for the steel surface since it was painted and was thus very similar to painted hard plaster, the absorption coefficient of which has been measured at the laboratory and found to be about 0·015. A figure for the absorption coefficient of the aluminium surface is more difficult to estimate. Measurements made by Davis and Evans$^{(3)}$ by the stationary-wave method have indicated that a metal surface may absorb between 0·2 and 1 per cent of the energy of a wave incident normally. An empirical relation obtained by these authors shows that the absorption coefficient for reverberant sound (such as was used for the transmission measurements above described)

Table 1. Comparison of calculated and observed increases in sound-reduction caused by rendering absorbent the interior of a double partition made of aluminium weighing 0·3 lb./ft^2

Frequency (c./sec.)	Thickness of partition 8 in.				Thickness of partition 4 in.	
	Increase due to absorbent felt		Increase due to fibre board		Increase due to absorbent felt	
	Calculated	Observed	Calculated	Observed	Calculated	Observed
	db.	db.	db.	db.	db.	db.
2000	13	11	7·5	6	11	10
1000	12	9	6	5	9·5	10
800	11	7	5·5	2	8·5	5
400	6	4	3·5	0	4·5	3
200	3	4	2	0	1·5	2·5

would be considerably larger. It is not likely, however, that it would be larger than the figure for painted steelwork. A figure of 1 per cent was accordingly chosen for calculating the results shown in table 1. The values used for the absorption coefficients of the fibre board and absorbent felts and the sound-reduction factor of a single sheet of aluminium are given in table 2.

Table 2

Frequency (c./sec.)	Sound-reduction due to single sheet of aluminium (db.)	Absorption coefficient of absorbent felt	Absorption coefficient of fibre board
2000	27	0·7	0·2
1000	22	0·8	0·2
800	20	0·7	0·2
400	15	0·4	0·2
200	8	0·4	0·2

The absorption coefficients used were based upon Eyring's formula although coefficients based upon Millington's formula would have been in better accord with the method of derivation of equation (3). These coefficients were not obtainable, but the small differences between the coefficients obtained from the two formulae are not likely to have an appreciable effect upon the results given below.

The sound-reduction factor of a single sheet should have been obtained while the sheet actually formed part of the double partition. There does not seem to be any way of obtaining this figure, however, except by using equation (3) above. Accordingly the figure obtained from one sheet alone was used. As $1/R_1$ and $1/R_2$ are at most frequencies small compared with α_1 and α_2, and in any case the spacings used were wide so that coupling effects would not be large, it is likely that the error thereby introduced is not serious.

Whilst the agreement between the measured and calculated values is fairly good, the calculated figures are, on the whole, somewhat larger than the observed. It would be possible to obtain better agreement by somewhat increasing the assumed values of the absorption coefficients for aluminium, but in the absence of reliable figures for these coefficients it is really not possible to say more than that formula (1) is capable of predicting the effect of an absorbent lining to a fair approximation but that there is no evidence to show whether it can be regarded as exact.

A more reliable check on the formula is obtainable by comparing the 8-in. partition lined with fibre board with the same partition lined with absorbent felt, for the absorption by the aluminium surfaces is then of no account. Assuming the same values for the absorption coefficients as before the results given below in table 3 are then obtainable.

Table 3. Increase in sound-insulation caused by substituting an absorbent felt lining for a lining of fibre board in a double aluminium partition.

Frequency (c./sec.)	Increase in sound insulation (db.)	
	Calculated	Observed
2000	5·5	5
1000	6	4
800	5·5	5
400	2·5	4
200	1	4

It will be seen that, allowing for the errors of measurement, which increase as the wave-length increases, there is reasonable agreement.

The conditions under which the experiments described above were made are, of course, exceptional and it is not likely, for instance, that a metal lining to a double window would occur in practice. However, surfaces of brick, plaster, painted plaster, or cement do very frequently occur in the interior of double partitions, for instance double windows. The absorption coefficient of the last-mentioned three surfaces is not likely to exceed 2 per cent, and hence the interior of any partition in which they occur may be highly reverberant as in the above experiments.

Bare brickwork is however more absorbent and it was therefore desirable to determine whether in this case also absorbent treatment would be advantageous. A set of measurements was therefore made in another pair of experimental rooms, in which the aperture has a bare brick surface. A double partition measuring approximately 5 by 4 ft. was formed from two sheets of iron sealed into the aperture at about 8½ in. apart. The iron weighed 21 oz. per square foot and thus the partition corresponded closely with a double window of 21-oz. glass.

The measurements of the sound-transmission through the partition were made with a technique differing in some respects from that used for the aluminium partition described previously. A beam of sound incident obliquely upon the partition was used and the note used was a pure tone, instead of a warble tone. The table below gives the increase in sound-reduction observed when the brickwork inside the partition was covered with absorbent felt having the absorption coefficients given in table 2. For comparison, the increase in sound-reduction calculated from equation (5) by the use of the absorption coefficients given for bare brickwork by W. C. Sabine and on the assumption that the iron has an absorption coefficient of 0·01 are also tabulated.

Table 4. Increase in the sound-insulating effect of a double sheet iron partition resulting from lining with absorbent felt the brick frame in which it was built. Weight of iron, 21 oz./ft^2

Frequency (c./sec.)	Sound-reduction factor of single sheet (db.)	Absorption coefficient of bare brickwork (W. C. Sabine)	Absorption coefficient of felt	Increase in insulation due to absorbent lining (db.)	
				Observed	Calculated
2000	37	0·049	0·7	13	11
1000	32	0·042	0·8	10	10·5
500	22	0·031	0·7	3	10
300	18	0·025	0·4	7	5·5
200	17	0·024	0·4	5·5	5

Owing to the use of a pure tone these measurements are subject to a greater uncertainty than those detailed in table 1. It will be seen that there is a definite gain when the brickwork is covered with absorbent and that quite satisfactory agreement between the calculated and observed figures is obtained. As a matter of fact equally good agreement is obtained if the iron sheets are assumed not to be absorbent.

§ 5. CONCLUSION

The results described above have practical significance since they indicate that by the use of absorbent treatment a double partition can be given a greater sound-insulating value, or alternatively that the same sound-insulation can be obtained by using a double partition of lighter construction, provided it is lined with absorbent. Thus double windows, as usually built with bare or plastered brickwork exposed between the two components, could always be considerably improved by covering the brickwork with absorbent. Similarly, to obtain the greatest effect from light double aluminium partitions such as are used in aeroplane construction, the interior surfaces of the aluminium should be covered with absorbent material. This, incidentally, would have the additional advantage of reducing noise due to drumming. It is evident, however, that the absorbent treatment should not completely fill the space between the two leaves of the partition, for this would tend to provide a mechanical coupling between the two components of the partition and thus to defeat the object for which it was inserted.

The experiments also suggest that double brick partitions would be improved by an absorbent lining. It is, in fact, quite a common practice to hang an absorbent blanket between the two leaves of such a partition. Experiments are in progress to test whether there is any advantage in this procedure. Other experiments have shown, however, that in such partitions the coupling between the two members is largely mechanical and takes place through the edges, whereas in the light partitions studied above the coupling takes place through the air between the members. Hence any effect due to an absorbent lining is likely to be small.

§ 6. ACKNOWLEDGMENTS

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THE DENSITY AND COEFFICIENT OF EXPANSION OF LIQUID GALLIUM OVER A WIDE RANGE OF TEMPERATURE

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ABSTRACT. Accurate measurements of the density and coefficient of expansion of liquid gallium at temperatures from 30° to 1000° C. have been made by a dilatometric method. The temperature was measured with a platinum resistance thermometer. An equation expressing the increase in volume as a function of the temperature has been found, and from that equation values have been calculated for the coefficient of expansion.

§ 1. INTRODUCTION

The element gallium, occurring in group 3 of the periodic system, has a melting-point of 29·8° C., and an unknown boiling-point greater than 1600° C.* In recent years, Andrade has developed a theory of the viscosity of liquids (1), and in connexion with this theory an accurate measurement of the kinematic viscosity of gallium from 30° to 1100° C. has been made by K. E. Spells (2) in this laboratory. Liquid gallium was chosen because of the big range of temperature over which it can be used. In order to calculate the actual viscosity it is necessary to know the density of the liquid over this temperature-range. Further, the variation of density with temperature of an elementary liquid over a wide range of temperature will clearly be of interest as soon as a satisfactory theory of liquids has been developed. The only previous density-determination for liquid gallium was obtained by Richards and Boyer (3), who carried out a research on the purification of the metal and measured the density of both the liquid and the solid at the melting-point, showing that the metal expands on solidifying.

The known chemical properties are that the metal readily oxidizes in air and is soluble in concentrated hydrochloric and nitric acids, forming two series of salts. It amalgamates with mercury and forms alloys with many metals. The oxide is non-volatile but is soluble in dilute hydrochloric acid with the formation of gallous and gallic chlorides, which have boiling-points of about 535° and 210° C. respectively.

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* Although there is no value for this boiling-point in the standard tables, there is a value of 2300° C. in the 1935 edition of Kohlrausch's *Praktische Physik*, but no reference is given.

§ 2. SOME PRELIMINARY MEASUREMENTS

As gallium is expensive only 4 cm.^{3} were available, and a few preliminary measurements of the mean coefficient of expansion were made with a pyrex-glass weight thermometer. It was necessary to fill this weight thermometer by a vacuum method, since the usual method of filling is impracticable for a liquid with such a high boiling-point, and the apparatus shown in figure 1 was made for this purpose. The weight thermometer A, made to hold about 2½ cm.^{3}, was fitted with a ground joint, so that it could be detached from the rest of the apparatus, and it was first calibrated with mercury.

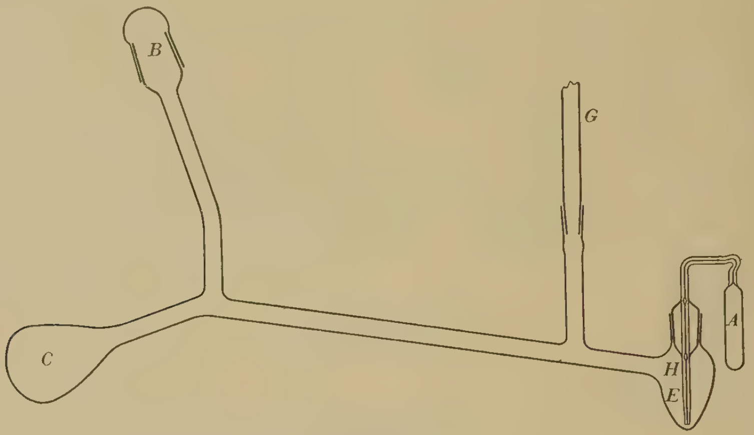

Figure 1.

The gallium was melted under dilute hydrochloric acid in a beaker and was poured into the bulb C through the opening B. The apparatus was evacuated through the tube G, when the remaining hydrochloric acid vaporized and was absorbed by solid potassium hydroxide. The gallium was then strongly heated to about 500° or 550° C., when the two chlorides volatilized and were deposited on the cool parts of the glass, leaving the gallium in a pure state. The metal then had the bright appearance of a globule of mercury, and flowed freely about the bulb C. This method of preparing gallium in a suitable condition was used by Spells⁽²⁾ and also, with a slight difference, by Boyer⁽⁴⁾. The thin film of chloride formed in the first instance by the hydrochloric acid protects the metal from oxidation during its transfer to the apparatus. The gallium in the bulb C was then tipped into the bulb E and gas was let in through the tube G, so that the gallium was forced up the capillary tube H into the bulb A. The gas used was specially pure hydrogen, which had been found to have no effect on gallium in the cold. The weight thermometer was now removed from the apparatus and a few readings were taken in the usual way by heating to a definite temperature and weighing.

The values obtained for the mean coefficient of expansion α (corrected to the temperature-range 32·38° to 310° C.), and for the density of the liquid at the melting-point, are given later. A few readings taken at 100° C. showed that the mean coefficient of expansion decreased with rise of temperature, the initial temperature being kept constant, but it was not possible to obtain accurate results over the smaller range as the weight of gallium expelled was small.

§ 3. THE DILATOMETRIC METHOD

In the experiments with the weight thermometer the method of filling was satisfactory, but with the measurements difficulty had been experienced owing to oxidation of the metal when it came into contact with air; hence a dilatometric method was adopted.

A quartz dilatometer in the form of a bulb and capillary tube was filled with gallium *in vacuo* and was heated in an electric furnace, the increase in height of the gallium meniscus being carefully measured. The dilatometer was calibrated with mercury. Three dilatometers were made for different temperature-ranges and the preliminary values obtained for the mean coefficient of expansion made it possible to calculate suitable values for their sizes.

The apparatus designed for filling the dilatometers is shown in figure 2. It was fitted on a board which could be turned about an axis through *C*. The portion of the apparatus beneath the joints *A* and *G* was made in quartz, whilst the upper portion was made in glass. The portion between the joints *A* and *B* was detachable and was made in triplicate with bulbs of different sizes at *D*. The dilatometer itself consisted of this bulb *D* together with the capillary tubes above and below, and would be sealed off at the points *E* and *F*. Five fine marks were made at equal intervals of 4 cm. on the capillary tube between *D* and *F*.

The tubes *H* and *J* were connected by short pieces of pressure tube to two vacuum systems. Tube *J* was connected to a Hyvac pump through tubes containing potassium hydroxide, phosphorus pentoxide, and calcium chloride: pure hydrogen could be admitted into this system. The tube *H* was connected to a two-stage mercury-vapour pump, through a liquid-air trap of the type designed by Andrade(5). The ends of the tubes *J* and *H*, and the ends of the fixed tubes leading to the vacuum systems, were brought near to the axis of rotation at *C*, so that the pieces of pressure tube were as short as possible. Two other short pieces of pressure tube, *U* and *V*, were included as shown to facilitate the fitting of the ground joint *A*.

The following experimental procedure was adopted for filling and sealing off the dilatometer. About 2 cm^3 of gallium were treated with hydrochloric acid and were placed in the bulb *N*; the apparatus was then evacuated. The gallium in the bulb *N* was heated to a bright red heat for about 45 min., so that the chlorides were driven off.* The gallium was then allowed to cool and was tipped into the bulb *O*, where it was again heated for about 15 min. This second heating was to remove any traces of chloride that the gallium might have picked up in passing from *N* to *O*. The two bulbs *D* and *S* and the capillary tubes between *F* and *Q* were thoroughly baked out by heating with a hand blow-pipe. The gallium was now tipped into the bulb R and the tap L was closed. A little hydrogen was then admitted through the tube J so that the gallium rose slowly up through the bulb S into the dilatometer bulb D, and finally entered the capillary tube above that bulb. Both the bulbs S and D were kept hot during the filling. The pressure was adjusted so that the gallium meniscus was a little way above the top of the bulb D, and then the dilatometer was sealed off at the points E and F. It will be noticed that during this filling and sealing off a high vacuum was maintained above the gallium in the dilatometer by the mercury-diffusion pump.

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* It is interesting to note that gallium is slightly volatile at this temperature (about 900° C.), and a very faint deposit of metallic gallium appeared on the hot parts of the bulb during the heating.

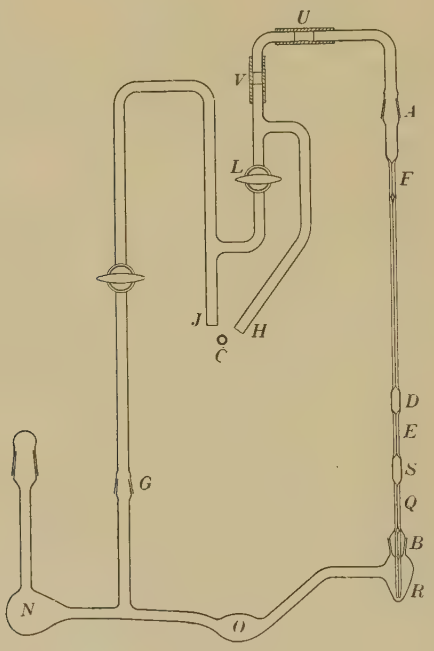

Figure 2.

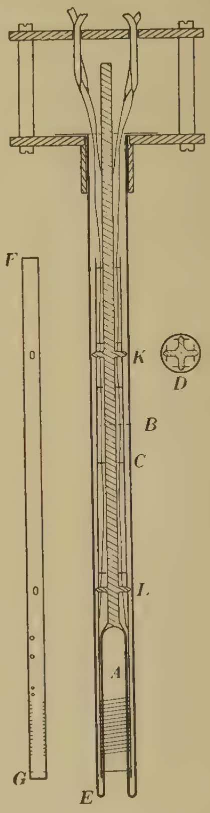

Figure 3.

The gallium dilatometer filled in this way was very satisfactory; when it was heated and cooled, the gallium showed no signs of sticking, and in appearance the gallium was indistinguishable from mercury. When calibrated, the dilatometer could be used as a high-temperature thermometer; such thermometers have also been made by Boyer(4). Altogether three dilatometers were filled.

§ 4. MEASUREMENTS

For measuring the temperature a special platinum resistance thermometer, shown in figure 3, was constructed. The short quartz tube *A* was joined to a long quartz rod *B*, which had pieces of thinner quartz rod fixed to it in the form of two crosses *K* and *L*. Four mica strips, similar to the one *FG*, were fitted on to these crosses as shown in the section *D*. The thin platinum wire, which was specially pure, was carefully annealed and was wound in a spiral on the notches cut in the lower ends of the mica strips. The leads, which were of 22-gauge platinum wire, were kept in position by pieces of mica placed around the rod *B*; the compensating leads were joined by a short length of the wire used for the coil. A quartz tube *C* was slid over the assembled structure, and the two tubes *A* and *C* were sealed together at the bottom *E*. A brass head, waxed on to this outer tube at the top, held the flexible copper leads, which were soldered to the platinum leads. These flexible leads were connected to a Callendar and Griffiths bridge, and the thermometer was calibrated in ice, steam, and sulphur vapour. The constants found were as follows:

$$\frac{R_{100}}{R_0} = 1\cdot3905 \text{ and } \delta = 1\cdot50,$$

where R_0 and R_{100} are the resistances at 0° and 100° C. respectively, and δ is the usual correction factor. These values are in accordance with the standard specification (6).

The dilatometer and resistance thermometer were now heated together in an electric furnace. The resistance thermometer was used upside down, so that the end *E* projected vertically upwards into the furnace, and the bulb of the dilatometer then fitted into it so as to be surrounded by the coil of platinum wire. Copper filings were packed into the remaining space in the tube *A*. A close-fitting thick-walled copper tube, of about the same length as the quartz tube *A*, was slid over the end *E* of the resistance thermometer to prevent any temperature-gradient along the quartz.

In order to be able to read the position of the gallium meniscus in the capillary tube of the dilatometer and at the same time to heat the capillary tube as uniformly as possible, a subsidiary furnace was placed on the top of the main furnace. This subsidiary furnace was provided with two quartz windows, each about 2 cm. long and 0·7 cm. wide, through which a direct view of the stem of the dilatometer could be obtained. Readings were then taken as follows.

The two furnaces being at the required temperature, the height of the dilatometer was adjusted so that both the gallium meniscus and one of the marks on the stem of the dilatometer came into view through the window in the top furnace; such an adjustment was always possible, because the length of the window was 2 cm. and the distance between the marks on the dilatometer was 4 cm. The height of the gallium meniscus above or below the visible mark was then measured with a cathetometer. It was found impossible to keep the temperature perfectly constant, and a series of readings of temperature and meniscus was taken over a period of about half an hour; these meniscus readings were then corrected to one temperature and their mean value was found. The mean heights thus obtained, together with the corresponding temperatures, are recorded in table 1; the heights are given as the total height above the initial mark. The negative sign indicates that the gallium meniscus was below this mark. The results for each dilatometer have been arranged in the order of increasing temperature, although actually they were taken in a random order; for instance, several of the points at other temperatures were taken between the two points at 235° C. The other columns of this table will be explained later.

Table 1

Dilatometer	Temperature (° C.)	Height (cm.)	Stem correction (cm.)	$\frac{V_2}{V_1}$
First	32·38	0·0108	—	1·00000
	299·92	5·2015	0·0567	1·03176
	346·45	6·0498	0·0661	1·03702
	427·53	7·5712	0·0378	1·04610
	476·94	8·4676	0·0492	1·05164
	571·76	10·1845	0·0364	1·06207
	651·71	11·5894	0·0365	1·07071
	732·17	13·0151	0·0412	1·07941
Second	32·38	− 1·2327	—	1·00000
	99·77	0·9349	0·0038	1·00834
	100·07	0·9470	0·000	1·00838
	160·25	2·8275	0·0009	1·01565
	190·81	3·7499	−0·0009	1·01923
	235·10	5·0689	−0·0023	1·02436
	235·37	5·0802	0·002	1·02440
	382·68	9·3088	0·0043	1·04114
Third	32·38	− 0·5057	—	1·00000
	685·71	8·9726	0·0106	1·07450
	880·69	11·5638	0·0192	1·09495
	1005·0	13·329	0·016	1·10876

In order that the results which were obtained with the different dilatometers might be compared, it was necessary to take a reading at some convenient reproducible low temperature near the melting-point of gallium, and the transition temperature of sodium sulphate, which is known to be 32·38° C., was chosen for this purpose. The first reading for each dilatometer was therefore taken at this temperature, the dilatometer being immersed directly in the melting salt. This reading was repeated after some of the readings at the higher temperatures had been taken, and the results showed that it remained unaltered.

With the two furnaces arranged as described, the temperature of the stem of the dilatometer was not uniform. This caused a small error in the observed height, and a correction for it was obtained as follows. If the temperature of the bulb of the dilatometer is t_1°, the temperature of any short length of the stem dl is t_2°, and the mean coefficient of expansion of gallium over the range t_2° to t_1° is α, then the correction to be added to the observed height is $\int \alpha (t_1 - t_2)\, dl$, the integral being taken from the level of the gallium meniscus down to the bulb, where the difference in temperature becomes zero. This difference in temperature was measured with a thermocouple and a graph was plotted for each observation. The value of α can be assumed to be constant over the range of temperature involved in any one correction, and hence the value of the integral is easily obtained from the graph. The corrections obviously had to be obtained by successive approximation, and each correction is recorded under the heading "stem correction" in the fourth column of table 1. In the case of the first dilatometer the corrections are larger than in the cases of the other two, because the upper furnace was not used and hence there was a big temperature-gradient along the stem.

With the three dilatometers the complete range of temperatures from 100° to 1000° C. was covered. Readings with the first dilatometer were taken at temperatures from 300° to 730° C. The second dilatometer, which had a larger bulb, was used at temperatures between 100° and 380° C.: the points at 100° were taken with a hypsometer. The third dilatometer was designed for temperatures up to 1000° C.; with this one, however, only a few points were obtained, because the quartz devitrified at the high temperatures and it was then difficult to read accurately the height of the gallium meniscus. Owing to a slight defect in design, the resistance thermometer had to be rewound and recalibrated after the measurements with the first dilatometer.*

One remarkable property of gallium, which can conveniently be mentioned here and which was very noticeable during this work, is the great tendency of the metal to supercool. Two of the dilatometers were left at room-temperature for several months after the measurements had been taken, and the gallium still showed no signs of solidifying.

§ 5. CALIBRATION

The capillary tubes and the bulbs of the dilatometers were calibrated with mercury, and the distances between the reference marks on the capillary tubes were measured with a travelling microscope. The second and third dilatometers were calibrated before they were filled, but the first dilatometer was not calibrated until after the readings with it had been taken. A value for the density of gallium was obtained with the first dilatometer.

The capillary tube *E*, figure 2, was made so fine that any uncertainty as to its diameter at the point where it was sealed off produced a negligible error in the total volume of gallium.

§ 6. RESULTS

The results in the fifth column of table 1 are given as the ratio V_2/V_1, where V_1 is the volume of gallium at the initial temperature 32·38° C. and V_2 is the volume at a higher temperature t. Values for the coefficient of expansion of the quartz were taken from the tables.

By the method of least squares, the following equation has been found for the ratio V_2/V_1:

$$\frac{V_2}{V_1} = 0{\cdot}99587 + \frac{1}{10^6}(128{\cdot}40\,t - 0{\cdot}03780\,t^2 + 0{\cdot}00003401\,t^3 - 0{\cdot}00000001250\,t^4) \quad \ldots(1).$$

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* The figures given on p. 704 are for the second calibration.

The coefficient of expansion, $V^{-1}\, dV/dt$, was calculated from the above equation, and values for it are plotted against temperature in figure 4. It is also possible to calculate from equation (1) the mean coefficient of expansion between 32·38° and t°, defined by $(V_2 - V_1)/V_1\,(t - 32{\cdot}38)$; this has been done for $t = 310$°, and the value is compared below with the corresponding value obtained with the weight thermometer.

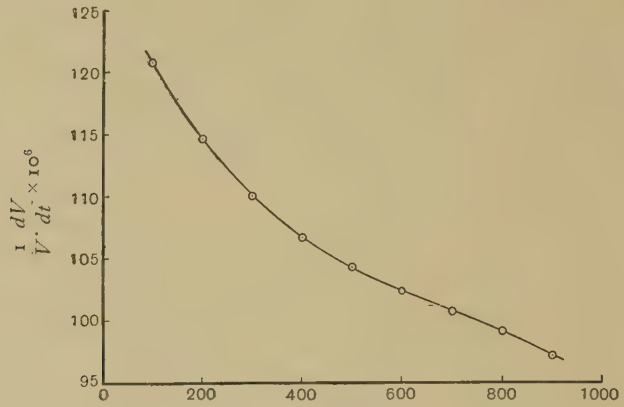

Figure 4.

Coefficient of expansion calculated from equation (1) ...	$118{\cdot}7 \times 10^{-6}$ per °C.
Weight-thermometer value	$118{\cdot}4 \times 10^{-6}$ per °C.

The values obtained for the density[*] of gallium, corrected to 29·8° C., are as follows:

Density by weight thermometer	6·0946 g./ml.
Density by first dilatometer	6·0953 g./ml.
Mean density at 29·8° C.	6·0949 g./ml.
Value obtained by Richards and Boyer at 29·8° C. ...	6·0947 g./ml.
Density at 32·38° C.	6·0930 g./ml.

Values for the density of gallium at temperatures up to 1000° C. can be calculated from equation (1).

§ 7. ACKNOWLEDGMENTS

The author wishes to express his thanks to Prof. E. N. da C. Andrade, both for suggesting this problem and for his valuable help and advice throughout the work.

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[*] The density of mercury at 0° C. has been taken as 13·5955 g./ml.

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(6) See, for instance, Callendar and Hoare, *Correction Tables for use with Platinum Resistance Thermometers* (1933).

DISCUSSION

Mr J. A. Hall. I have been specially interested in the author's very neat design of the resistance thermometer, but there are one or two points which are not made quite clear in the diagram. What are the dimensions of the bulb, and in particular the width of the annular space in which the wire is wound? Are any precautions taken to prevent convection in the stem, such as the use of mica washers adopted by Callendar? It is a common fault to regard these merely as insulators, and to neglect their function as baffles. The diagram does not make it clear to me whether such baffles have been used. Has the author made any measurements of the lag constant of the thermometer? Quite apart from the special needs of the present experiments, the type of construction would seem to have advantages in minimizing lag. I do not care for the use of flexible leads with a thermometer of this type, and would prefer the use of light single-strand cable. It seems to me that the author has been a little optimistic in recording temperatures of about 800° C. to an accuracy of 0·01° C., for his constants appear to have been determined with an accuracy only sufficient to give the temperature to about 1 part in 1000. In any case, there is at present no evidence that the resistance-thermometer scale can be laid down with certainty to such a high accuracy at these temperatures.

Author's reply. The outside diameter of the tube *C* of the resistance thermometer was 2 cm., and the width of the annular space between the tubes *A* and *C* was $2\frac{1}{2}$ mm.; the length of the inner tube *A* was about 9 cm., and the length of the coil itself was 3 cm. Several pieces of mica, which can be seen in the diagram, were placed around the rod *B*, and, as Mr Hall points out, they should be regarded both as insulators for the leads and as baffles to stop convection currents. It is, however, a little doubtful whether their function as baffles is as important in this type of thermometer as it is in the usual type, because the presence of only a small annular space in the lower part of the thermometer must be of considerable help in eliminating the convection currents around the coil. I did not make any measurements of the lag constant of the thermometer. With regard to the accuracy of the temperatures given in table 1, the bridge could be read to 0·01 °C., and the temperatures have been recorded to this accuracy because the last figure in the temperature-measurement corresponds to the last figure in the height-measurement; for instance, in the case of the first dilatometer a change of 0·01° C. in the temperature is equivalent to a change of 0·0002 cm. in the height of the gallium meniscus. The absolute accuracy of the temperatures is, of course, limited by the accuracy of the calibration; the error increases with rise of temperature, and at the highest temperature (1005° C.) it is about 1 part in 1000.

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THE DETERMINATION OF ABSOLUTE UNITS

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ABSTRACT. The International Committee on Weights and Measures, in announcin the forthcoming change of electrical units and in forecasting the values of the ratio between the new and the old units, do not say how these ratios are to be determined There are good reasons for silence; but if the matter is to be discussed at all, it should b discussed completely.

There are two problems involved, one that of the object to which the new units ar directed, the other that of the means by which that object is to be attained. The resolution (not having the full sanction of the Committee) which accompany their statement, mus be interpreted as concerning the first problem alone, if they are to be regarded as reasonable and relevant. The object of this paper is to consider the second.

For this purpose one of the many alternative methods, by which the national physica laboratories might proceed to calibrate the units, is selected and analysed with a view t determining exactly what experimental laws will be used, and how the arbitrary assumptions, necessary to fix the units, are introduced in connexion with them. The result i shown diagrammatically.

The argument leading to it is given on pp. 711–17.

Both in their identity and in their interrelations the propositions set forth in thi figure are very different from those usually set forth in discussions of how absolute units are, or ought to be, determined. It is suggested that the difference is significant and i *prima facie* evidence that the usual expositions are incomplete and attain their apparen simplicity only by concealing difficulties and complexities.

§ 1. INTRODUCTION

In a recent statement* the International Committee of Weights and Measures fix the date on which "the actual substitution of the absolute system of electrica units for the international system shall take place". They says that "In collaboration with the national physical laboratories, the Committee are actively engaged in establishing the ratios between the international units and the corresponding practical absolute units"; and it gives provisional values for these ratios.

Nothing is said of how the Committee and the laboratories are going to determine the ratios. Silence on this point might well be justified on the ground tha anyone conversant with the matter knows what procedure they will adopt, excep possibly in respect of minor details that it is inconvenient to specify beforehand But there is some evidence that it was due to another cause, namely disagreemen within the Committee; for the statement is succeeded by certain resolutions which

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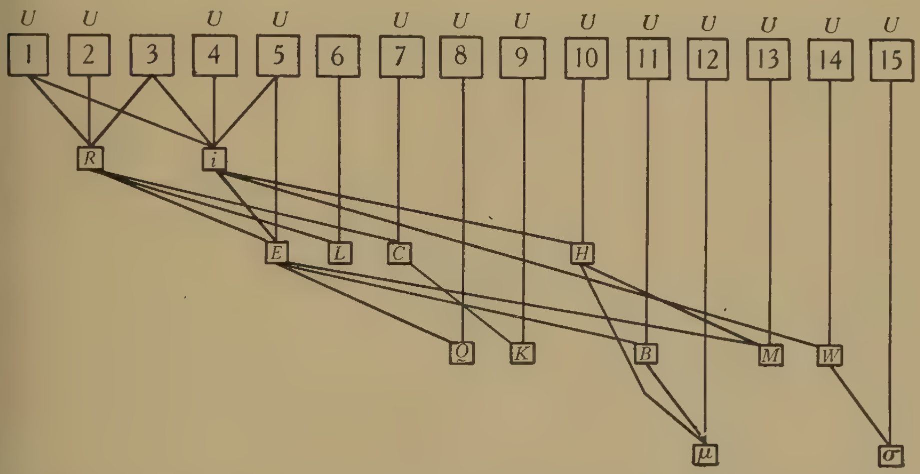
* The quotations here and below are from the Appendixes to a paper by R. T. Glazebrook *Proc. phys. Soc.* 48, 444 (1936). They are apparently authentic; but the full documents should b read if it is desired to ascertain how far the quotations from the resolutions mentioned presently represent the views of the Committee.

(if they have any relevance to the matter) would seem to suggest a procedure by which the ratios might be determined. The Committee do not apparently take full responsibility for the resolutions; but it appears that the following sentences express opinions entertained by at least some of their members:

(*a*) "The connexion between mechanical and electrical units should be secured by assigning the value 10^{-7} in a non-rationalized m.k.s. system...to the quantity generally known as the 'permeability of space'."

(*b*) "The definitions for the principal electromagnetic units might run as follows. *Ampere*. The ampere is the constant current which, if maintained in two straight parallel conductors of infinite length at a distance of one metre apart in empty space, produces between these conductors a force equal to 2×10^{-7} m.k.s. units of force per metre length...."



1, $L=10^{-7}.\iint\frac{\cos\epsilon\, ds\, ds'}{r}$; 2, $\omega.dL/d\theta=R$; 3, R (and c) additive; 4, $F=i^2\, dL/d_3$; 5, $R.i=E$; 6, $jpL=R$; 7, $j/pC=R$; 8, $CE=Q$; 9, $C/C'=K$; 10, $i/l_h p=H$; 11, $E=B.\omega.dS/d\theta$; 12, $B=\mu H$; 13, $Fl=MH$; 14, $Ei=W$; 15, $W=\sigma.m.dT/dt$

It is not surprising that these propositions did not win universal acceptance. (*a*) seems to violate the elementary principle that, in order to fix the units of N quantities, N arbitrary assumptions must be made. For the Committee propose to fix at least 7 electrical units, and (*a*) make only one arbitrary assumption over those fixing the mechanical units. (*b*) proposes to jettison all the accurate methods of determining the ampere that have been worked out by generations of physicists.

The explanation is, doubtless, that the resolutions confuse the object of determining absolute units with the means by which that object is to be attained. Absolute units are such as give to the constants in "fundamental equations" convenient values, e.g. 1 or 4π or a power of ten (see further below). The problem of their object is to make the best choice of these equations and of the constants in them; the problem of the means is to find an experimental procedure whereby any given system may be assigned a value in terms of the units fixed by this choice.

Statement (*a*) apparently refers only to the object; it may be interpreted as meaning that, of the seven arbitrary choices, six are to be made on the "absolute principle", while the seventh is to be made by the alternative method of assigning a numerical value to some property of some prescribed system, namely the permeability of space. Statement (*b*) apparently refers to the means; but then (with great respect) it is nonsense. It would be sensible if it said that one of the choices was to be made so that the fundamental equation relating to the force between two current elements to their relative position has a prescribed form and prescribed constants. This equation, with six others implied similarly in the part of (*b*) which has not been quoted, would then fix the seven arbitrary choices.

If the units were to be determined entirely afresh, the problem of the object would be of great importance; but since the Committee have clearly decided not to change existing units by more than a few parts in ten thousand, it is of no importance at all, because the solution is already fixed. It is clear that all that is proposed is to give exactly convenient values to those constants which now have approximately convenient values, the constants and the equations in which they occur are already chosen.*

But the problem of the means, which may be termed *calibration*, remains important. It involves a conception entirely foreign to the problem of the object, namely precision or freedom from experimental error. Connected with any set of fundamental equations is a set of experimental laws, which may be regarded as consequences of them. Of these laws some are of far greater precision than others. The problem is to select a group of laws, each at least as precise as any possible alternative, which is sufficient for all the necessary calibrations.† Thus there are many experimental laws that follow from Ampère's law, Faraday's law of induction, and Ohm's law, all of which are equivalent in principle for the calibration of the ohm. But, among these, two stand out in precision, namely that of the Lorenz experiment and that giving the relation between a calculated inductance and a resistance. These are therefore to be preferred to others.

When these experimental laws have been selected, they—and not the fundamental equations—become the immediate basis of the units. In these days, when the foundations of our physical faith are liable to be shattered at any moment, the distinction is not wholly unimportant. It may be true that if (for example) we founded our units on the Lorenz experiment and then discovered that it was not a con-

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[*] One reason why discussion of the object continues so fiercely appears to be that the combatants believe that theorists will actually use the important equations in the form appropriate to the official units, and that, therefore, by inducing the Committee to choose particular units, they can force everyone to adopt the form of these equations that they prefer. But their belief is utterly unfounded—fortunately so, as I believe. Theorists express their equations in such a form as to be free from constants irrelevant to their particular argument; the constants that are irrelevant depend on the argument. Thus the same writer will sometimes write Coulomb's law in a form in which the electronic charge is 1, sometimes in a form in which the velocity of light is 1. No fixing of practical units—with which he is not directly concerned—will make him abandon this convenient and excellent practice. Those who are so anxious that everyone should toe the line they draw are wasting their time in arguing with International Committees; the only thing that will achieve their purpose is severe penal legislation imposed by national governments.

[†] This is why objection is taken to statement (*b*). Of the consequences of the fundamental equation, that selected is known to be far inferior in precision to others.

sequence of the fundamental equations, the whole problem of units would be reconsidered, and that therefore it is unnecessary to consider this possibility. Nevertheless, there seems to me some interest in inquiring what are the experimental laws that are likely to form the true basis of the units that the Committee propose to adopt. That inquiry is the main purpose of this paper.

Strictly it should include a consideration of all the good alternative methods for the absolute determination of the ohm, ampere, etc. But my concern is with principles rather than with details; I want to inquire whether the experimental laws that will be the immediate basis of the units can be arranged in some sort of logical scheme, such as is often proposed for the fundamental equations which may be held to form their ultimate basis. Accordingly only one way of calibrating the units will be discussed; it will suffice if it is a reasonable method and likely to form part at least of the actual method, which will doubtless embrace many alternatives. Further, some instructions concerning the object of the units must be assumed. It will be assumed that they are contained in statement (*a*), as interpreted above, and that "non-rationalized" implies that the "convenient value" is always to be 1. Lastly, some quantities will be introduced into the scheme other than those discussed by the Committee, and it will be assumed that all of these are also to be determined by the absolute method.

§ 2. THE EXPERIMENTAL LAWS

It will be well to start by considering generally how an experimental law determines a unit by the assignment of the value 1 to a constant. The process may be described as follows.

We find a number of systems S and a piece of apparatus into which each of them can be inserted in turn. The systems must be identifiable and distinguishable. The distinction may be made by the varying values of a measurable property possessed by each of them, so long as the measurement of this property does not involve the law under consideration; on the other hand it may be made by properties which are not measurable. S

The apparatus must be characterized by two measurable properties x, y, and by an identifiable state P (which is usually some form of equilibrium) assumed, for a given value of x, when and only when y has some particular value. P

We insert each system S in turn in the apparatus, and determine the pairs of values (x, y) for which the apparatus assumes the state P. We find on examination that these pairs of values are related by the algebraical equations

$$f(x, y) = C \qquad \text{......(1),}$$

f, C

where C differs according to the member S inserted and C_r is characteristic of the member S_r. C is then a measurable property of the systems S. C_r S_r

The value of C_r depends upon the units used in measuring x, y. We may express this fact by rewriting (1) thus

$$f(x, y) = C'.X \qquad \text{......(2),}$$

C'

and adopting the convention that, when the units of x, y are changed, only C' is to be changed. X_r is then a characteristic of the system S_r only. There is still an ambiguity; for C_r can be divided into C' and X_r in many ways. This ambiguity can be resolved by two methods. One is to choose arbitrarily some system S, say S_1, and assign to it some value X_1 (say 1); then C' is determined by facts. Alternatively we may choose arbitrarily one pair of units of x, y, and assert that C' has some value, say 1, for these units; then *every* X_r is determined by facts. Absolute systems of units are those in which the second procedure is adopted widely (though not always universally).

It is to be observed that the symbol = in equation (1) expresses far more than a numerical relation; it implies also the nature of the apparatus and the state P. Again, in an absolute method, the system S_1, to which the value 1 is attributed, is not distinguished in any way from other systems S. Neither of the terms "equation" and "unit" indicates accurately the essentials of the procedure.

No complete system of measurement can be established by this process alone; for the process implies that some properties, namely x, y, are already measurable. Somewhere in the background must lie another process, depending on laws that are not numerical. These are always laws of addition, which state that certain combinations of two system S are equivalent, in a special sense, to a third member; such laws are the basis of all measurement, but do not themselves involve measurement. Laws of this kind are often used in conjunction with numerical laws, of the type (1), in a manner that will appear from the example we are going to discuss; it is fatal to overlook them.

We can now start on our task of attempting to order in the light of these principles a procedure that the standardizing laboratories might adopt in establishing their calibrations. Of course it is impossible, in a reasonable space, to set forth the matter completely; only the salient features will be discussed.

The instructions assume that we can measure mass, length, and time, and assert (as three of the arbitrary assumptions) that the units are to be the kilogram, metre, and second. We shall have to assume further (though much might be said on the matter) that it follows necessarily that we can measure force, power, angle and area; the units of force and area must be 10^5 dynes and the square metre. We introduce at once the fourth assumption prescribed explicitly by defining a quantity L appertaining to a pair of linear conductors of, and surrounded by, non-magnetic material. At present this is a pure definition; but it becomes a physical assumption as soon as we use the definition. The definition of L is

L

ϵ, s, r

$$L = 10^{-7} . \iint \frac{\cos \epsilon \, ds \, ds'}{r} \qquad \text{......(3).}$$

The meaning of the symbols is too well known to be stated; it has only to be observed that L can be determined by measuring lengths and angles alone. We can also measure $dL/d\theta$ and dL/dz, where θ represents rotation of one conductor in relation to the other while z represents relative translation, for a determinate value of θ or z.

θ

z

But a question naturally arises. How are we to know whether materials are conducting or non-magnetic? It has to be admitted that there is no evidence that we could ever have arrived at our present methods of determining these matters without a knowledge of laws to be introduced later. But such knowledge is not essential in principle. For the determination requires no measurement; we have merely to introduce the material into suitable apparatus (different according as we are inquiring into conductivity or permeability), and notice whether there is any change; we have not to measure the change. Again, in order to decide what apparatus is suitable, we cannot require a knowledge of the absolute units we are seeking; for our present ideas on the subject were fully developed before any question of absolute units arose. Accordingly, though it would be very difficult to explain the method without circular arguments, it is almost certain that the task is feasible. Similar questions arise at almost every stage; they will not be mentioned again.

Resistance. We now start our first experiment (Lorenz apparatus). The systems S (resistors) are bodies identified as individuals. Of a pair of linear conductors to which L appertains, we connect one, A, in series with a source of current (which need not be measured) and with each S in turn; and we connect the other, B, in a circuit, containing a galvanometer. Joining the ends of S*, P means that no current passes through the galvanometer. That defines the apparatus. If we measure ω, ω
the relative angular velocity of A and B, we establish the law

$$\omega\,.\,dL/d\theta=C \qquad \text{......(4).}$$

The assumption made is that we are to write $C=1\,.\,R$; R (ohms) is then a measurable R
property of the resistors.

This method of measuring R is precise only when R lies within a certain range. To measure R for all resistors, we must establish the additive properties of R. We discover that we can find triplets, S_1, S_2, S_3, such that if S_1 and S_2 are connected in series, they are equivalent to S_3 in the sense that the substitution of one for the other produces no change in a suitable apparatus. We find further that, in virtue of this fact we can assign numerals s to the resistors consistently, so that in such a triplet $s_1+s_2=s_3$. If we assign the numeral 1 arbitrarily to one resistor, we can then measure a property R' of the resistors, quite independently of equation (4) or any R'
other numerical law.

We now find that, in the range within which equation (4) is applicable, R' is proportional to R; if we use for R' the unit that we have established for R, R' and R are identical. In a similar way we discover the additivity of conductivity c, and c
make c equal to $1/R$. In future we use equation (4) only to establish the unit; all measurement in terms of this unit is done by the process depending on the additivity of resistance and conductivity.

Current. In our second experiment the systems S are silver voltameters in which silver is deposited at different rates; since we can measure mass and time, these can be identified. The apparatus is a balance by which forces can be applied

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* The use of the radius of a disc for B is a more practical device, which requires no special consideration.

z F along z between the two linear conductors to which z refers; P is equilibrium; a voltameter S is in series with both conductors. If we measure the force F and dL/dz, we can establish the law

$$F = C\,.\,dL/dz \qquad \text{......(5).}$$

i The assumption made is that we are to write $C = 1\,.\,i^2$; i (amperes) is then a measurable property of the voltameters. We may proceed, if we wish, to prove that i so measured is proportional to the rate of deposition of silver within a certain range; but this law is not essential to the procedure.

The fact that the proportionality is not universally valid (e.g. for very large currents) suggests that again we should use equation (5) only to establish the unit, and use some other law for measuring i. But it is not now convenient to use a method based on addition. Actually i is additive in branched circuits; but measurement based on that property is inconvenient and not precise. We must leave this problem for the moment. But it is to be observed that we can justify our decision i' to write $C = i^2$, rather than $C = i'$, on the ground that i, defined by the first convention, and not i', defined by the second convention, is additive, and is therefore the more important quantity. However, this example makes it clear that the application of the convention of absolute measurement requires more than the decision to make constants unity; it requires also the choice of the function of the measurable quantity which that constant shall multiply. Accordingly if an absolute system is to be expounded completely, the convention implied should be stated explicitly *in every case*.

Potential-difference. The systems here are voltaic cells. The apparatus need not be described. Measuring R and i by the methods already established, we find

$$R\,.\,i = C \qquad \text{......(6);}$$

E in accordance with the absolute convention we take C (volts) as being the measurable property E of the cells. E turns out to be additive for cells connected in series; this proposition is used in accurate measurement, but it is not required to extend the range of E. For since a resistor having any value of R can be obtained, all E's can be measured by means of a current within the voltameter range. However we can use equation (6) to extend the range of current-measurement, and yet base our extension of the meaning of current on facts and not on a mere definition. For if we write equation (6) thus

$$E/R = C \qquad \text{......(6}'\text{),}$$

we can prove that this law is valid outside as well as inside the voltameter range, if currents outside can be identified, and thus measure currents by a method valid over a much wider range. This is the actual process of measurement; equation (5) merely defines the unit.

It would be tedious to proceed throughout with the same deliberation. The remaining quantities will be discussed more summarily, and many questions, similar to those already raised, will be ignored.

Inductance. The unit is defined by equation (3) applied to certain simple forms. Measurement in terms of this unit depends upon the law

$$jpL = R \qquad \ldots\ldots(7),$$

which can be proved, and needs no arbitrary assumption.

Capacity. Here, on the other hand, the law*

$$j/pC_0 = R \qquad \ldots\ldots(8),$$ C_0

both defines the unit, by the assignment of the value 1 to the constant, and provides the method of measurement.

Quantity of electricity is both defined and measured by suppressing the constant in the law

$$C_0V = Q \qquad \ldots\ldots(9).$$

Dielectric constant. We define a geometrical quantity C_0' ("electrostatic capacity *in vacuo*") for some simple condenser; among geometrically similar systems it is proportional to length. We establish the law that C_0' is proportional to C_0, as just defined; the constant ratio C_0/C_0' is defined as the dielectric constant. Of course it does not turn out to be 1 for a vacuum. C_0'

Magnetic quantities. These present some difficulty. The International Committee propose to fix only one magnetic unit, namely the weber, the unit of flux ϕ. Concerning the remainder there appear to be unresolved differences concerning the object of the units. Thus those directly interested do not seem to be agreed by what fundamental equations the gauss and the oersted ought to be related to the other units and to each other, or (what comes to the same thing) what quantity if any these names should denote. I shall therefore merely assume that quantities usually denoted by B and H are to be defined somehow by the absolute method, that is, by assigning a convenient value to constants in an experimental law; but I shall give them no name and shall leave undetermined the convenient value Z in the experimental laws I shall choose. Incidentally this procedure has the advantage of making it clear that the absolute method is not really confined to the choice of 1 (or even of 1 and 4π) as the convenient value. ϕ Z

A further difficulty is that magnetic quantities are vectors. A mass of verbiage would be necessary to state the matter accurately; the assumption that all quantities are similarly directed will simplify the statements greatly and will mislead nobody; accordingly I shall make it.

The only systems for which calibrations in respect of H and B will be required are systems of magnets producing fields uniform over a considerable volume. We start by defining a geometrical quantity $1/l_h$, characteristic of a linear conductor, which in similar systems is inversely proportional to length. Various formulae for it are given, all equivalent in the relevant cases. One of them is l_h

$$1/l_h = \int \mathbf{ds}' \times \mathbf{r}/r^3 \qquad \ldots\ldots(10).$$

We establish the law that, if the arrangement of magnets and the linear conductor are placed in suitable relative positions, and if l_h and the current i through the linear conductor are varied, then, in the state P such that no couple is exerted on a suitably placed magnet,

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* C_0 is written with a suffix for capacity, in order to distinguish it from C in equation (1).

$$i/l_h=C \qquad \ldots\ldots(11).$$

H We write $C=Z.H$.

We next take a coiled linear conductor, whose turns embrace effectively the area S. We place this conductor in the field of the arrangement of magnets, rotate it at angular velocity ω and measure the potential difference E between its ends when the normal to the effective area is in some fixed direction relative to the arrangement. We establish the law

$$E=C.\omega.dS/d\theta \qquad \ldots\ldots(12).$$

We write $C=Z.B$.

If, in a given arrangement of electromagnets, we vary i, the magnetizing current, and measure B and H, we find that, within a certain range,

$$B=C.H \qquad \ldots\ldots(13).$$

μ We write $C=Z.\mu$.

If we place a magnet in a variable field H, we establish the law, valid within a finite range,

$$F.l=C.H \qquad \ldots\ldots(14),$$

where $F.l$ is the couple on the magnet. We write $C=Z.M$. M is then the magnetic moment.

There remains the weber, the one magnetic unit that the Committee do propose to fix. I can find no experimental law of any reasonable precision in which flux ϕ is a constant. Thus the resolutions mentioned above propose that the weber is to be "the magnetic flux which, when linked with a circuit of a single complete turn, would produce in that circuit an electromotive force of one volt if reduced to zero in one second at a uniform rate". But, if we have not measured flux, how are we to determine whether its rate of reduction is uniform? And, even if this difficulty could be overcome, a flux which is being reduced at a uniform rate is clearly not a constant of an experimental law describing that experiment. Perhaps there is a way of avoiding this difficulty; but meanwhile it appears that flux ϕ must be regarded as a mere name for the quantity $\int BdS$, the selection of that name not being dictated by any simple and unitary experimental law. If this is so, the assignment of a value to the weber is only a roundabout way of assigning a value to C in equation (12), which defines the unit of B. Accordingly no more need be said about it.

The watt. We establish the law that if the passing of a current i through a potential-difference E generates the same amount of heat (i.e. produces the same thermal change) as the dissipation of W watts of mechanical power, then

W

$$E.i=W \qquad \ldots\ldots(15).$$

This is a universal law, valid for all systems to which it applies at all; there is no constant C variable with the system, and therefore no call for any arbitrary assumption concerning its value. However, there is something arbitrary in giving a special name to the product Ei, rather than to any multiple of it; accordingly the definition of the watt as Ei may be taken (though with some hesitation) as one of the arbitrary assumptions of our system.

However, the important matter in practice is the relation of the watt to some quantity used in calorimetry, say the specific heat of water; this is what requires calibration. We establish the law

$$W=C.m.dT/dt \qquad \ldots\ldots(16),$$

where m is the mass and T the temperature of water in the neighbourhood of (say) 15° C. The specific heat of water is the quantity obtained by writing $C=1.\sigma$ in this equation. (The measurement of temperature has to be assumed, but this is not an electrical quantity.) σ, T

§ 3. DISCUSSION

The survey that has been made is summarized in the diagram. Here the large numbered squares are the quantitative propositions that have been used; they are identified by their numerals on the right. Purely qualitative propositions, such as were discussed on p. 713, are ignored. Those propositions in which an arbitrary assumption is made for the purpose of fixing units are distinguished by a *U*. The quantities discussed are denoted by the small squares; lines connect them to the propositions on which their measurement depends. They are arranged in generations represented by the horizontal rows, such that a quantity in one generation depends on at least one quantity in the previous generation. It will be observed that the only two propositions on which all the quantities depend are the definition of mutual inductance and the additivity of resistance (and conductivity); neither of these is a numerical law, and neither of them therefore involves the assumption of absolute measurement in its typical form.

There is evidently a profound difference, not only in identity, but also in interrelation between the laws that form the immediate basis of any experimentally determined units and the fundamental equations (which I should term "theory") that are so often offered as their ultimate basis. We have found no evidence that "it is possible to deduce all electrical quantities from (one single quantity) by means of a series of equations in each of which one and only one new electrical quantity appears".* The relations that we have found are much more complex, and would be more (and not less) complex if we had taken account of all the alternative procedures that will doubtless play some part in determining the Committee's final choice of the ratios.

From this difference many persons will probably draw the conclusion that we should fix our eyes steadily on these beautifully simple relations and ignore all the untidy and unpleasant work that the staffs of the national physical laboratories will have to perform for our benefit. But my conclusion, though the need for brevity forbids me to support it fully, is very different. It is that all this beautiful simplicity is delusive and attained only by ignoring essential matters. If we were so indelicate as to inquire precisely what these equations mean and what is their relation to experiment (surely they must have *some* relation), the stately fabric would disintegrate; it would be found that that simple "=" covers a multitude of complexities, and that many propositions are implied that are not expressible by so-called equations at all. The illogicalities discussed on p. 713 would reappear, not in the crude nudity of the "classical" exposition,* but still merely half-hidden behind decent coverings. There may be no logic of science—I do not think there is—but there is yet a distinction between sound and thorough exposition of the foundations of measurement and summaries that are specious merely because they are full of circular and fallacious arguments.

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* These are the words of a correspondent quoted by R. T. Glazebrook, *Proc. phys. Soc.* **48** (1936), 452.

DISCUSSION

Dr E. H. Rayner. We are all glad to see Dr Campbell and to have a paper by him on such a subject as the philosophy of units.

In the first place I do not think that Dr Campbell's definition of absolute units on the second page of the paper agrees with the recognized meaning of the term. He says that "absolute units are such as give to the constants in 'fundamental equations' convenient values, e.g. 1 or 4π or a power of ten". Actually the meaning of the term "absolute" was defined by the B.A. Committee in 1863 as follows:

> "The word 'absolute' in the present sense is used as opposed to the word 'relative' and by no means implies that the measurement is accurately made or that the unit employed is of perfect construction; in other words it does not mean that the measurements or units are absolutely correct but only that the measurement, instead of being a simple comparison with an arbitrary quantity of the same kind as that measured, is made by reference to certain fundamental units of another kind treated as postulates."

This paragraph is reproduced by the late Sir R. T. Glazebrook in a note on the three absolute systems of electrical measurements.†

Dr Campbell is under a serious misapprehension when he imagines that the work of scientists over many years is to be scrapped. The reverse is the case. The present so-called international units are only of a stop-gap character. They are quite empirical, being defined in terms of the rate of deposit of a mass of silver in an electrolytic cell and of a nominal value which is ascribed to the specific resistance of mercury. They were adopted to achieve a high measure of agreement between the units of different nations. The units so obtained are intended to be very nearly the same as the corresponding absolute units, which are the ideal but have not until recently been realized with adequate accuracy on account of the technical difficulties involved. The absolute units which are to come into force in 1940 will be in no way dependent on the present units, as Dr Campbell imagines. The approximate values of the ratios which he mentioned have been published in order to prepare the public and the instrument-makers for the change.

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* The classical exposition starts from charges and poles. How a charge is to be distinguished from a pole is never explained, except possibly by the statement that poles do not exist.

† *Proc. phys. Soc.* **48**, 450 (1936).

As an example of the alteration involved, a resistance of 100,000 ohms according to the present size of unit will be approximately 100,050 ohms in absolute units. Every resistance will have to be shortened to acquire the same numerical value in the new unit. The significant figure after the 5 may be more definitely given at a later date.

As Dr Campbell says, writers in many countries have discussed the electrical units and their basis during the last few years. As regards the mode of realization, few of those who have been writing on the subject have seen instruments for generating the units, and still fewer have handled them. While philosophical discussion of the subject is all to the good, it must not interfere with or dictate the method of realization. The recent literature on the subject has not in any way modified the methods of realizing the units, as carried out in the few national laboratories cooperating in this work.

No standard method is prescribed, such as is necessary to obtain a high degree of agreement in realizing the present empirical units. In fact the apparatus for generating the ampere and the two methods for generating the ohm at the National Physical Laboratory are unique. No other Laboratory uses the Lorenz machine or the Campbell mutual-inductance method for the ohm, and no one else uses a Kelvin type of balance. Other nations are using the Rayleigh pattern. All the balance methods require a knowledge of the local value of gravity.

In practice the basic quantity is inductance, which has the dimension of length only, and the value is arrived at from linear measurements of the apparatus, which have to be determinable with high precision. To arrive at the unit of resistance the dimension of time has to be added. This is done as a speed of rotation of part of the apparatus in the Lorenz machine and as an alternating-current frequency in the Campbell method. It happens that resistance is one of the most important scientific and engineering electrical quantities, and portable realizations of it over a very wide range of values can be constructed with high precision. The fundamental unit as realized is at once the basis of the most important technical quantity.

For the evaluation of current in absolute measure, the quantity *force* has to be dealt with, and it requires the addition of the dimension mass. The great sensitivity available in a balance has led to its use for the measurement of the electromagnetic forces. The force available is small, only of the order of 1 part in 1000 of the dead weight carried by the balance; but the perfection of the apparatus enables it to be measured to the order of 1 part in a million. In practice, however, a portable ammeter, accurate to the order of 1 in 100,000 or in 10,000, is not available, so that the ampere is not a practicable engineering reference unit. Simple electrolytic cells of great stability and reproducibility of voltage happen to be available. Their voltage is determinable in terms of the absolute ampere and ohm, whence they are universally employed as practical standards of voltage; and they form the second engineering type of portable unit.

Dr L. Hartshorn. As one who is closely concerned with attempts to determine electrical units with precision, I have long felt that the experimental foundation for the fundamental laws of our text-books was by no means obvious. Dr Campbell's exposition is the only one I have ever met which could claim to be based on facts of the kind which can be verified with the precision expected of a modern electrica laboratory. I am reminded of an attempt I made some three or four years ago to write out definitions of the ampere, ohm and volt in terms which could be upheld in either an electrical laboratory or a court of law. After reading Dr Campbell's paper I was sufficiently curious to look up these attempts at definitions and I think that of the ampere is sufficiently in line with Dr Campbell's argument to be worth quoting.

> "*The ampere* is the tenth part of that unvarying electric current which, when traversing each of two linear circuits having a common axis of symmetry and located in free space, causes them to act upon one another with a force the value of which expressed in dynes is numerically equal to the rate of change of mutual inductance of the two circuits with respect to a displacement of one relative to the other along the common axis of symmetry. *The mutual inductance* of two linear circuits in free space is given by the following integral extending round both circuits
>
> $$\iint \frac{ds.ds' \cos \epsilon}{r},$$
>
> where ds refers to an element of one circuit, ds' an element of the other, ϵ is the angle between the two elements and r is the distance between them."

Although this definition satisfied me at first, as not involving unit poles or abstractions remote from actual experience, I was subsequently disturbed by the reflection that the linear current which is implied, and which Dr Campbell also uses, is an abstraction which can never be realized. If we use very thin wires in order to approximate more closely to the conception we introduce another difficulty: the resistance of the wire increases and therefore the electric field associated with any current through the wire becomes sufficiently important to disturb any measurements of the kind in which the magnetic effects only are wanted. I should be interested to know how Dr Campbell would deal with these difficulties. Possibly they would appear as a limitation to the accuracy of verification of equations (7) and (8), but I can well believe that even with such a limitation these laws have been verified with a higher accuracy than could be claimed for possible alternatives.

I well remember the late Sir Joseph Petavel's comment on my proposed definitions. It so well summed up my own feelings on the question. He merely said in the pleasantest possible manner "I hope it won't be necessary to use them." If I were a member of the International Committee on Weights and Measures, I think I should feel exactly the same about Dr Campbell's scheme, although from a purely scientific point of view I am entirely in agreement with it. What such a committee should say is partly an administrative question, and it is at least arguable that since the pronouncements of the committee are mainly intended to coordinate the measurements of workers in various countries, they will be most effective if expressed in terms of the current working ideas, and, in the case under discussion, the simple generalizations of our text-books, with all their concealed difficulties and complexities. However, the Physical Society is far more concerned with the foundations of scientific knowledge than with the problems of standardization, and there can be no question that this paper goes a long way towards clearing away the debris from the foundations of electrical measurements.

I observe that Dr Campbell discourages the idea of a definitive system of units for all purposes. I agree that theorists should continue to express their equations in such a form as to be free from constants irrelevant to their particular argument, and this means that they should be free to vary their units as may be convenient. However, I feel that it would be a great convenience to scientific workers if all numerical data were expressed in terms of one preferred system, and if the equations corresponding to this system were employed universally for theoretical work of a technical character, which must ultimately deal with numerical values of the quantities of ordinary laboratory experience. I do not see any advantage in the use of the electrostatic and electromagnetic c.g.s. systems along with the practical system for such work, and I think that experimental physicists and electrotechnicians would find it convenient to have one preferred system on the lines proposed by Giorgi and G. A. Campbell. It is regrettable that the recent flood of literature on the subject is such as might discredit the proposal.

Mr J. Guild. I must strongly support Dr Campbell's contention that it is the experimental laws underlying practical methods of measurement which give significance to the results of measurement and not the "beautifully simple relations" and abstract concepts on which the significance is usually assumed to depend. This would also appear to be the view of the late Sir Richard Glazebrook, as I interpret his paper on the fourth unit of the Giorgi system of electrical units,[*] admirably summarized in his last sentence: "We must distinguish between methods of measurement...and the mathematical theory of electricity." I believe that a clearer understanding of the meaning of measurement—and therefore of the significance of the quantitative data on which all theory of the behaviour of things has to be based—would be brought about if the official definitions of important scales of magnitude were shorn of all reference to ideal systems which, in the nature of things, cannot exist, and which have no relevance to the sordidly practical problems of measurement. I think we have gone too far, in the past, in the attempt to rid our metrical systems of what Dr Rayner describes as "the trammels of empiricism". It seems to me that to attempt to rid measurement of empiricism is to attempt to rid it of its essential characteristic. Measurement is necessarily empirical if it is to fulfil its purpose of providing quantitative data which shall be independent of any theory into which those data may subsequently be fitted. Its empirical nature should be advertised and not concealed by a veil of abstractions which, far from lending dignity to measurement, imposes on it the indignity of sailing under false colours.

The practical object of arriving at a choice of units which will avoid the occurrence of arithmetically awkward factors in physical relations involving the more

[†] *Proc. phys. Soc.* **48**, 452 (1936).

important magnitudes is, as Dr Campbell points out, a mere matter of convenience having nothing to do with the rightness or wrongness of the units selected. The aim has gradually been achieved, to an ever increasing order of accuracy, by the process of trial and error in the standardizing laboratories, and cannot be achieved any other way, definitions notwithstanding.

Author's reply. Dr Rayner is right in saying that, in 1863, the object for which absolute units were proposed (and from which they derived their name) was the avoidance of any need for material intercomparisons; the assignment of values to arbitrary constants was a mere means of attaining the object. But the object has proved unattainable, because intercomparisons are more precise than absolute determinations; the assignment of the constants has therefore become the primary object. The statement of the International Commission is, in effect, an instruction to the standardizing laboratories to choose their material standards, by comparison with which all measurement will actually be made, so that the constants approach the assigned values within the least possible experimental error.

I cannot discover in my paper any signs of the delusions of which Dr Rayner suspects me. One of my main purposes is to point out that eminent persons do not always mean what they say.

Dr Hartshorn's point about linearity is interesting. The ideal conditions contemplated by simple theories can never be realized, but departures from them may be concealed by experimental error. Whether they are concealed in any particular case is a question of fact. Thus if, when we calculate L on the assumption that the conductors are linear, we find systematic errors, not concealed by experimental errors, in laws (4) and (5), then, and only then, we must make "corrections" for non-linearity by using a more complicated theory. The simple scheme proposed then breaks down; but the main conclusion, that the relation between units and fundamental equations is very complicated, is confirmed. It is interesting to note that one of the propositions that would have to be added is that currents are additive.

Unless it is seriously proposed to change the units by large factors, in order to produce a set that everyone can be persuaded to use, the questions how far uniformity is desirable and how it may be attained are irrelevant to this discussion. The best way to secure that all numerical results shall be stated in the official units would be the publication of a very complete conversion table, which would take into account all the forms of the fundamental equations that anyone is likely to use. Conversion tables published hitherto have always been incomplete, because the author's main aim has been to argue that some particular form is better than others; moreover, the tables have been confused by obscure irrelevancies about dimensions.

I agree entirely with Mr Guild.

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THE STRUCTURE OF SOME METALLIC DEPOSITS ON A COPPER SINGLE CRYSTAL AS DETERMINED BY ELECTRON-DIFFRACTION

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ABSTRACT. Nickel, copper, zinc, cadmium, silver, chromium and cobalt were deposited electrolytically on etched copper single crystals and the structure of the deposits was found by electron-diffraction. At small current densities the layers are oriented except in the case of zinc and cadmium. The nickel and cobalt deposits give patterns containing additional spots, lines and irrational spots. It is shown that these are accounted for by assuming the occurrence of repeated twinning on (111) planes, the additional spots being due to twinned lattices and the lines due to twin planes. The twin planes must be considered separately and not simply as part of the lattices on either side of them. The thin sheets of lattice thus formed give rise to the irrational spots observed. Finally, a discussion is given of the factors determining the orientation of a layer of metal on the copper crystal.

§ 1. INTRODUCTION

The oriented overgrowth of one crystal on another is well known in the case of ionic crystals. Similar phenomena occur with metallic crystals and may often be investigated very conveniently by means of X rays⁽¹⁾ or electron-diffraction. Using the latter, G. P. Thomson⁽²⁾ showed that a copper compound is oriented in a definite way on the etched face of a copper single crystal. Later, Farnsworth⁽³⁾ deposited silver on a gold crystal and found that the silver film had the orientation of the gold crystal. Cases have also been reported by Finch and Quarrell⁽⁴⁾ where a deposited metal suffers a change from its usual lattice dimensions in order to conform, across the contacting planes, with the underlying material.

The continuance of the structure of the underlying metal by the deposit has also been studied in other ways. Blum and Rawdon⁽⁵⁾ showed clearly, by the microscopic examination of etched sections, that the crystal grains at the surface of a piece of cast copper were continued by a deposit of electrolytic copper. Later workers have shown that this phenomenon also occurs when the deposit and the base are of different metals⁽⁶⁾.

The present paper describes the results obtained when various metals were deposited on the etched face of a single crystal of copper. G. P. Thomson's method of attack was again employed and the deposition was accomplished by electrolysis of the usual electroplating solutions.

Before proceeding to describe the experiments, reference will also be made to the results of Kirchner and Lassen(7). They evaporated silver on to a rock-salt cleavage face and examined the surface by electron-diffraction. The results showed that the silver was oriented as a single crystal with its cube face parallel to the rock-salt cleavage plane. The pattern from the silver consisted generally of the usual cross grating of spots. For some thicknesses of silver, however, certain of the spots observed were not in the positions to be expected but occurred, for example, in groups of four, symmetrically placed around the normal positions. These spots were named *irrational spots* and an explanation of their appearance was given by Kirchner and Lassen, who showed that they could be considered as arising from octahedral planes acting as cross gratings inclined to the electron beam. It was also suggested that the octahedral planes, being most densely packed with atoms, would tend to act in this way. This matter is referred to later in the sections dealing with nickel and cobalt.

§ 2. GENERAL EXPERIMENTAL PROCEDURE

The electron-diffraction apparatus was of the well-known Thomson-Fraser(8) type with a camera-length of 28 cm. The crystal specimens were cut from a rod 6 mm. in diameter. The surfaces of the specimens were ground on 0000 emery paper and etched for 5 min. in a 10-per-cent solution of ammonium persulphate. They were washed for a few seconds under tap water, then placed in alcohol and finally in benzene. Before the plating of the specimens, diffraction photographs* were taken from the copper surface alone to ensure that this was perfectly clean. These photographs showed the usual cross grating of sharp spots. The first specimen cut also showed Kikuchi lines, but these did not occur in later specimens. G. P. Thomson(2) has shown that the cross-grating pattern is due to small projections on the crystal surface, these projections or lumps being crystallographically coherent with the main crystal. He has also discussed the fact that etched metal crystals do not as a rule show Kikuchi lines and he attributed this to distortion of the lattice(9). Since a copper single crystal is rather soft, it was found difficult, in the present experiments, to avoid slight bending of the rod during sawing. This did not appear to result in any change in the spot patterns, but evidently, according to Thomson's theory, the distortion produced must have been sufficient to cause the disappearance of Kikuchi lines.

The plating circuit was of simple type and the anode of the plating cell was a cylinder of the same material as the metal being deposited except in the case of chromium, in which a lead anode was used. The composition of the various plating solutions is stated later at the end of this section. These solutions do not present any features worthy of special mention. There was no agitation of the solutions during plating and the operations were carried out at room-temperature. In many cases it was evident that Faraday's laws of electrolysis did not apply and the thickness of the deposited layer could not be determined in this manner. In most cases the thickness stated must be regarded as only approximate.

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* These, and later photographs, were taken with the beam at almost grazing incidence on the surface of the specimen.

Details of the various plating solutions and anodes are given in the table.

Table

Metal	Plating solution in g./litre	Anode
Ni	300 $NiSO_4.6H_2O$ 3·1 NaCl 6·2 H_3BO_3	Ni
Cu	200 $CuSO_4.5H_2O$ 30 H_2SO_4	Cu
Zn	96 $ZnSO_4.7H_2O$ 4 NaCl 6 H_3BO_3	Zn
Cd	400 $3CdSO_4.8H_2O$ 3·5 NaCl 7 H_3BO_3	Cd
Ag	0·26 $KAg(CN)_2$ 0·02 KCn	Ag
Cr	400 CrO_3 2 H_2SO_4	Pb
Co	300 $CoSO_4.7H_2O$ 3 NaCl 6 H_3BO_3	Co

§ 3. NICKEL ON COPPER CRYSTAL

Experiments performed. In all cases the etched (110) face of the copper single crystal was used as base. (i) A film of nickel of 20 A. thickness was deposited at a current-density of 0·3 mA./cm.^{2} The electron-diffraction pattern showed spots as in the original copper pattern and also faint rings due, apparently, to polycrystalline nickel. Similar effects were observed for thicker films of nickel deposited at the same current-density. When 200 A. had been deposited, the rings and spots were approximately equal in intensity. (ii) The current-density was increased to 3·25 mA./cm.^{2} and the results were similar to those obtained at 0·3 mA./cm.^{2} (iii) The current-density was increased to 10·5 mA./cm.^{2} and the deposit was of the same nature as in the first two cases. (iv) The current-density was lowered to 0·025 mA./cm.^{2} No rings were observed in the resulting diffraction patterns. When 50 A. had been deposited, the pattern was the same as that obtained from the original copper, but when the thickness of nickel was increased, new characteristics appeared. These were best studied in the two important azimuths of the (110) face (*a*) when the electron beam was approximately parallel to the diagonal of the cube-face, and (*b*) when the electron beam was approximately parallel to the edge of the cube. When 230 A. had been deposited, there was no change from the normal pattern in azimuth (*b*) except a slight loss of sharpness in the spots. In azimuth (*a*), however, there were lines running through the spots, forming a diamond-shaped pattern, and additional spots lying on these lines, figure 6. The lines became more and more prominent as the thickness of the nickel was increased still further to several thousand angstroms and this was accompanied by a small amount of elongation in some of the additional spots, in the direction of the lines on which they were situated. When 1000 A. had been deposited, the pattern in azimuth (*b*) was completely changed from its normal form. Each spot was replaced by two irrational spots placed vertically one above and one below the normal position, figure 7. (v) At a current-density of deposition of 0·015 mA./cm^2, the results were the same as at 0·025 mA./cm^2

Explanation of results. It appears from (i), (ii) and (iii) that, when nickel is deposited on the etched face of a copper single crystal at current-densities of 0·3 mA./cm^2 or more, the layer of nickel is polycrystalline with the usual face-centred cubic structure. The rings appear to pass through the copper spots in the case of thin layers, so that it must be presumed that the first layers of nickel have the same lattice constant as copper. Measurements (based on the formulae $d=L\lambda/r$ and $\lambda=h/mv$) on a plate taken from a layer of nickel 500 A. thick gave a value for the lattice constant of 3·58 A., which seems slightly high compared with the X-ray value of 3·517 A. Doubtless the nickel gradually reaches its normal structure as the thickness is increased.

The results obtained at low current-densities, (iv) and (v), show that, for small thicknesses of the order of 60 A., the nickel is oriented in exactly the same manner as the underlying copper single crystal. In the case of greater thicknesses, of 1000 A. or more, it will be convenient to consider the two principal azimuths separately. The pattern obtained with the beam parallel to the cube-face diagonal is best regarded as made up of five parts. These are indicated by circles, triangles, squares, full lines and dotted lines in figure 1. Certain of the spots, indicated by black circles, for example those lying on the line *ab*, are common to two or more patterns. Underneath the pattern in figure 1 is shown the (110) face of the specimen. This, as already explained, is not perfectly plane but covered with small lumps. In this particular azimuth a possible and indeed probable section of a lump on the (110) face is a small triangle bounded by (111) and (11$\bar{1}$) planes as shown in figure 1. The electron beam is considered to be moving in a direction normal to the plane of the paper. The other bounding faces of this lump may be left undefined. The pattern of spots indicated by circles is clearly due to nickel forming on the various lumps in conformity with the copper (main pattern). The pattern indicated by squares may best be regarded as arising from layers on the octahedral face *AB* This pattern may be derived from the main pattern by revolving the main pattern through 180° about the line *ab*. In this case, the spot *d* of the main pattern becomes the spot *e* of the pattern of squares. Alternatively, the spots of the main pattern may be reflected across the line *ac*, produced if necessary. It is at once seen tha spot *f* of the main pattern then becomes spot *g* of the pattern of squares. The line *a* is perpendicular to *ab* and parallel to the octahedral plane *AB*. The pattern indicated by small squares is therefore formed from a nickel lattice twinned on (111) planes o previously deposited nickel (Spinel twin). In the same way it can be shown tha the pattern indicated by small triangles, figure 1, arises from nickel twinned on $(11\bar{1})$ planes, such as *CD*. To obtain the line pattern indicated by full lines, figure 1, we require a plane of atoms lying parallel to the electron beam and normal to the direction of the lines. Since the lines lie perpendicular to the face *AB* this suggests that the twin plane is acting alone to produce the line pattern. The fact that the twin pattern and the line pattern increase in intensity together as the thickness of the layer is increased indicates that the two are connected, and suggests that repeated twinning is occurring in layers parallel to *AB*. Moreover, since the lines appear to increase in intensity slightly more quickly than the twin spots and since the twin spots become somewhat drawn out, it is evident that the successive twinning layers are becoming thinner as the thickness of the deposit is increased. Similar considerations apply to the pattern of dotted lines. It is not at first clear why the twin planes should act alone and not simply contribute to the spot patterns. If, however, the equilibrium of atoms in the twin plane is considered, it is seen that they differ from atoms in the interior of a face-centred cubic lattice. Normally a given atom in the lattice has twelve nearest neighbours surrounding it, lying uniformly distributed on a sphere with the given atom as centre. But an atom in the twin plane is not uniformly surrounded by its nearest neighbours. This is seen in figure 2 (*a*), which shows a (111) plane *AB* seen edgeways, i.e. looked at along

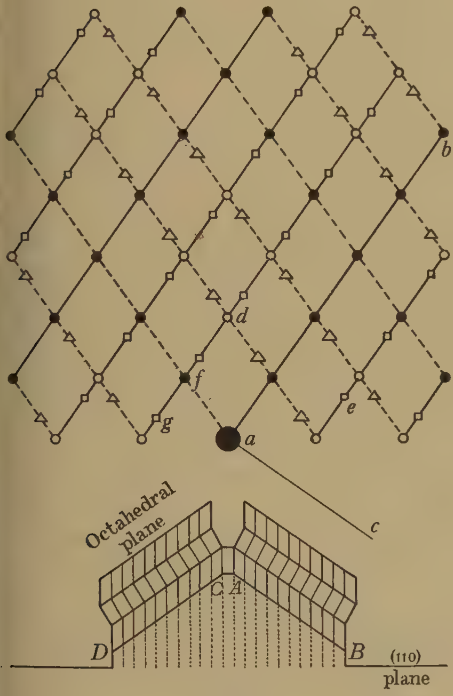

Figure 1.

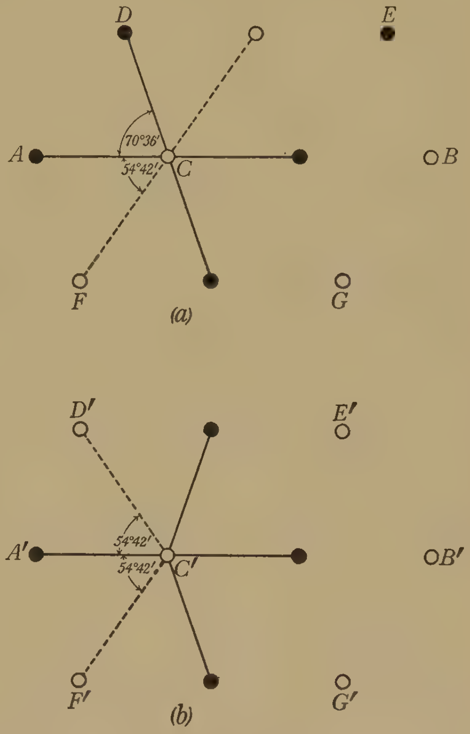

Figure 2.

a diagonal of a face of the cube. The circles are to be regarded as representing atom in the plane of the paper and the black spots as atoms in planes immediately abov and below the plane of the paper. DE and FG are (111) planes on either side o AB in an ordinary face-centred lattice. It is important to note that a black circl represents two atoms but a white circle only represents one atom, in figure 2.

In figure 2 (*b*), the (111) plane $A'B'$ is seen acting as a twin plane. The asymmetrical position of the atom C' in the twin plane $A'B'$ is immediately seen o comparing its position with that of the atom C in the normal lattice. The atom C has six nearest neighbours lying to the right and only four to the left. The remainin two neighbours of C' are immediately above and below it. The result must be tha the atoms in the twin plane undergo a slight shift to attain equilibrium and thi causes the twin plane to be detached, as regards its diffraction pattern, from th lattices on either side of it.

The pattern obtained when the beam is parallel to the edge of the cube must b considered as arising from the structure deduced above. The beam is now paralle to the (110) plane and lying in the plane of the paper in figure 1, lower diagram Since the successive layers on the octahedral faces of the small projecting lum have been deduced to be very thin (only just sufficient to yield an extended spo pattern in the previous azimuth) it appears that in the new azimuth they will ac merely as cross gratings inclined at an angle of 35° 18′ to the beam. The patter from layers on AB, figure 1, will consist of spots lying at the intersection o (1) lines normal to the shadow-edge, and (2) ellipses with their major axes normal to the shadow-edge. The equation to these ellipses is of the form

$$\frac{\xi^2}{\dfrac{B^2-AC}{A}}+\frac{(\zeta-B/A)^2}{\dfrac{B^2-AC}{A^2}}=1.$$

$O\xi$ and $O\zeta$ are axes lying in the plane of the plate, $O\xi$ being parallel and $O\zeta$ normal to the shadow-edge. The origin is the central spot of the pattern. A, B, C are defined by

$$A=\cos^2\alpha_0-\tan^2\alpha\sin^2\alpha_0,$$

$$B=L\sin\alpha_0\cos\alpha_0(1+\tan^2\alpha),$$

$$C=L^2(\sin^2\alpha_0-\tan^2\alpha\cos^2\alpha_0),$$

with $$\frac{\sqrt{6}}{2}a(\cos\alpha_0-\cos\alpha)=n\lambda, \qquad n=0,\ \pm 1,\ \pm 2, \text{ etc.}$$

where a is the lattice constant 3·6 A., $\alpha_0 \doteqdot 35° 18'$, L is the camera-length 28 cm., and λ is the wave-length 0·061 A. of the electrons. The radius of curvature at the end of the major axis (i.e. in the region actually seen on the plate) is $\sqrt{(B^2-AC)}$. When $n=0$ this gives 19·82 cm. but the zero order cannot be observed. Taking n equal to -2 results in the most suitable ellipse for comparison. The value of the radius when $n=-2$ is 15·4 cm. When an arc of a circle of this radius is drawn on tracing cloth, an excellent fit is obtained with the appropriate spots on the pattern, figure 7. The layers on DC, figure 1, will yield ellipses turned the opposite way.

The interference conditions of the layers on *DC* and on *AB* arising from rows of atoms normal to the beam and parallel to the shadow-edge are expressed by lines normal to the shadow-edge, and these are identical with one another and with the corresponding condition for the original copper. Thus the original side-spacing* is preserved but otherwise the pattern is quite different from that of the original copper. In figure 1, lower diagram, is shown diagrammatically the nickel deposit. The dotted-line shading indicates copper and the full-line shading nickel. Three layers of nickel are shown on each octahedral face, the middle layer being a twin.

Kirchner and Lassen's explanation of the phenomenon of irrational spots—namely, that the (111) planes, being most densely packed with atoms, act as cross gratings—does not appear to be tenable for, on this assumption, irrational spots would be expected in the patterns obtained from ordinary etched specimens of single crystal. The absence of the irrational spots in such cases suggests that they are associated only with deposited layers and that their explanation must be found in the disposition of the layers by the assumption of repeated twinning as indicated above.

Finally will be considered the question of the lattice constant of nickel deposited slowly on the etched copper single crystal. The normal value for nickel is 3·517 A. and for copper 3·608 A. Thus a film of nickel about 100 A. thick should give rise to a pattern of spots close to, but distinct from, the copper spots. No such doubling was observed. Actual measurements on six plates gave the value 3·60 ± 0·006 A., subject to a further uncertainty of about 0·5 per cent due to possible inaccuracies in measurement of camera-length, making the final result 3·60 ± 0·03 A. This is definitely in excess of the value for nickel but equal to that for copper within the errors of experiment. Thus it appears that the nickel, when it is deposited slowly, retains the lattice constant of the underlying copper. This expansion of the nickel lattice may be the cause of the twinning which is observed.

§ 4. COPPER ON COPPER CRYSTAL

Experiments performed. (i) A film of copper 6000 A. thick was deposited at a current-density of 0·75 mA./cm.² The electron-diffraction patterns showed no change from the original copper single-crystal pattern. (ii) A film of copper 20,000 A. thick was deposited at 3 mA./cm.² The same result was found as in case (i). In addition, it was observed that the spots were drawn out towards the shadow-edge. This effect was more pronounced when the thickness was increased to 40,000 A. Also, when the time of deposition had been long, fainter spots were seen, forming the same type of pattern as the copper spots but corresponding to a larger lattice constant than copper. These are evidently the spots obtained by Prof. Thomson(2) and explained by him as due to a copper compound such as Cu_2O. (iii) A film of copper 7500 A. thick was deposited at a current-density of 0·5 A./cm.² The resulting pattern consisted of rings due to ordinary polycrystalline copper.

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* By *side-spacing* is meant the spacing of planes normal to the shadow-edge and parallel to the beam of incident electrons.

Explanation of results. It appears from (i) and (ii) that when copper is deposited on the etched face of a copper single crystal at current-densities of 3 mA./cm.^{2} or less, the layer of deposited copper is oriented in exactly the same manner as the underlying single crystal. Also, when the thickness of the deposit is 20,000 A. or more, the diffraction spots are elongated towards the shadow-edge, indicating that refraction is taking place. Thus it may be deduced that the surface has become somewhat flat,* the flat portions being all parallel to the plane free surface of the crystal which is being examined. When the copper is deposited at 0·5 A./cm.^{2} there is no orientation and the deposit has the usual polycrystalline structure.

§ 5. ZINC ON COPPER CRYSTAL

Experiments and results. Deposits of zinc of various thicknesses were obtained with current-densities from 8 μA./cm.^{2} to 1 mA./cm.^{2} In all cases the diffraction pattern was due to ordinary polycrystalline zinc. At the low current-densities the diffraction patterns obtained from the deposits showed the effect of large grain-size.

§ 6. CADMIUM ON COPPER CRYSTAL

Experiments and results. As in the case of zinc the deposits all gave patterns of rings due to polycrystalline metal, even at low current-densities (30 μA./cm.^{2}).

§ 7. SILVER ON COPPER CRYSTAL

Experiments performed. Both (111) and (110) etched faces of the copper single crystal were used. (i) Silver was deposited for 18 hours at 15 μA./cm.^{2} The pattern showed both the original copper spots and spots due to silver. While the copper spots were sharp, the silver spots were really short arcs about 2 mm. long. There were also faint rings due to silver and these passed through the appropriate silver spots. (ii) Silver was deposited for periods of 34, 51 and 72 hours, at the above current density. The same features were observed as in (i), the copper spots becoming very faint with increasing thickness and the rings (due to polycrystalline silver) observed in (i) also became fainter. (iii) When silver had been deposited for 100 hours at 15 μA./cm.^{2} the pattern of spots was entirely due to silver and the silver rings were very faint. In the particular azimuth of the (110) face where the beam is parallel to the cube-edge there were observed, in the pattern, bands running parallel and normal to the shadow-edge and passing through the spots, figure 11. (iv) With a much stronger solution a quick deposit of silver was obtained by simple dipping. This gave a pattern showing rings due to silver and also to copper spots.

Explanation of results. From the above experiments it is seen that, when silver is deposited slowly on the etched copper single crystal, the silver takes the orientation of the copper crystal and gives a similar electron-diffraction pattern except that the normal lattice spacing of silver is retained. The explanation of the thick lines or bands in the pattern observed with a very thick deposit may perhaps be found by analogy with the optical effects obtained with cross gratings. When the number of scattering centres in an optical cross grating is reduced, subsidiary maxima appear in the diffraction pattern and these are not always found to be resolved. Thus they may give rise in the diffraction pattern to lines joining up the spots and of the same breadth as the spots. If the projections through which the electron beam passes were very small (i.e. from 5 to 10 atoms across) then we should expect the electron-diffraction pattern to show these effects; larger projections would give subsidiary maxima too faint to be visible.

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* See reference (9), especially page 647 and figure 2.

When silver is deposited rapidly on the copper crystal there is no orientation and only the ordinary polycrystalline rings are observed.

§ 8. CHROMIUM ON COPPER CRYSTAL

Experiments performed. No deposits were obtained at low current-densities such as had been used in depositing other metals. The plating took place rapidly at high current-densities and was accompanied by vigorous evolution of gas at the cathode. The (111) copper face was used. (i) Chromium was deposited at 0·2 A./cm.^{2} for 20 min. The pattern showed rings due to ordinary polycrystalline chromium. (ii) Chromium was deposited at 0·06 A./cm.^{2} for periods of time ranging from $\frac{1}{3}$ sec. to 20 sec. The patterns showed spots, some sharp, others on the same plate slightly drawn out into arcs. The pattern appeared in its most simple form when the beam was approximately parallel to the cube-face diagonal of the copper. The pattern then obtained, figure 10, showed two chromium azimuths simultaneously. This is illustrated in figure 3, where the spots from one azimuth are shown as circles and from the other as squares. (iii) Chromium was deposited at 0·06 A./cm.^{2} for 80 sec. The patterns showed spots as in (ii) and rings passing through the spots. (iv) Chromium was deposited at 0·2 A./cm.^{2} for $\frac{1}{3}$ sec. The results were the same as in (ii).

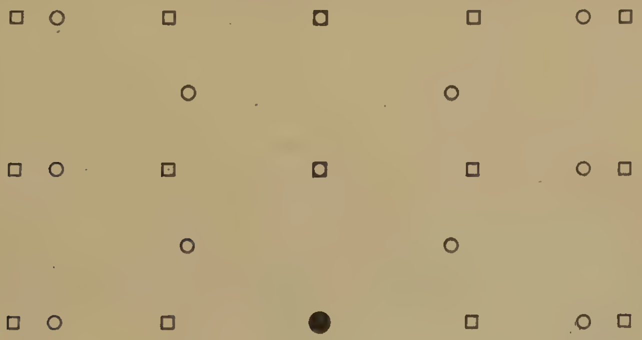

Figure 3.

Explanation of results. A thick layer of chromium on the copper crystal exhibits no orientation and has the ordinary structure of chromium. In the case of thin layers the patterns show at once that there is orientation with (110) planes of chromium, parallel to the (111) copper face, on which the deposit was made. The spacing of (110) chromium planes only differs by 2 per cent from that of (111) copper planes so that the spots on the centre line due to the chromium and unde lying copper must be almost superimposed. There was no doubt, however, tha the spots were due to chromium and not copper only, as the side-spacings wer quite different from the copper side-spacings. In order to explain why the tw chromium patterns occur simultaneously, figure 3, we must examine the azimuth which give rise to these. In figure 4 (*b*) and 4 (*c*) are shown chromium (110) plane If the electron beam is parallel to *CD*, figure 4 (*b*), we have the $\sqrt{2}$ side-spacing an

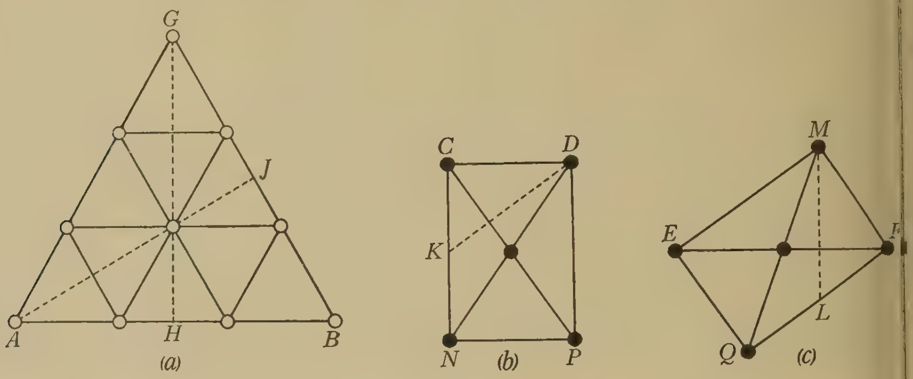

Figure 4.

obtain the pattern of squares shown in figure 3. If the electron beam is parallel t *EF*, figure 4 (*c*), then we have $\sqrt{6}$ side-spacing and obtain the pattern of rectangle indicated by circles in figure 3. Figure 4 has been arranged so that *CD* and *E* are parallel to one another and also to *AB*, the cube-face diagonal direction of th copper (111) face, figure 4 (*a*). The copper (111) face has been drawn to the sam scale as the chromium faces. The chromium (110) faces (*b*) and (*c*) must therefor be imagined moved up and placed on the copper (111) face (*a*), without any rotation This gives the orientation of chromium on the copper single crystal, with the cube edge or cube-diagonal of (110) chromium planes parallel to the cube-face diagona in the (111) copper plane.

§ 9. COBALT ON COPPER CRYSTAL

Experiments performed. The (110) etched face of the copper crystal was used a base. (i) Cobalt was deposited at 4 μA./cm^2 giving thicknesses of deposited meta of 8000, 16,000 and 24,000 A. as calculated by Faraday's laws of electrolysis. Th patterns obtained all showed the same features. They were similar to those obtaine from the copper crystal alone, but each copper spot in the pattern was replaced b two or four irrational spots according as the electron beam was parallel to (*a*) th cube-face diagonal or (*b*) the cube-edge. In the former azimuth (*a*) each spot wa replaced by two spots on either side of it, figure 8. In the latter (*b*) each spot wa replaced by two spots, one above and one below, and also by two spots, one o either side; the sideways separation in this case was much smaller than the vertical separation, figure 9. (ii) Cobalt was deposited at 50 mA./cm.^{2} for a few seconds. Rings due apparently to hexagonal and face-centred cubic cobalt were obtained. Some of the rings due to hexagonal (close-packed) cobalt were not found, but owing to the closeness of several of the lattice spacings this was not considered to cast any doubt on the deduction.

Explanation of results. The irrational spots obtained with cobalt deposits on the copper crystal are similar in some ways to those discussed by Kirchner and Lassen (7). In all cases the distances between associated irrational spots was greater towards the edge of the pattern than near the central spot, there being a continuous increase in the separation. The explanation must be similar to that laid down for nickel on the (110) copper face, except that additional octahedral planes must be called into account besides the two, (111) and $(11\bar{1})$, which were introduced in the discussion on nickel. We may suppose that the $(1\bar{1}1)$ and $(\bar{1}11)$ planes are also found as bounding faces of a small projection on the copper surface. These planes are normal to the (110) plane and would thus appear as steep vertical sides to the lump or projection considered, whereas the other octahedral planes make an angle of 35° 18′ with the (110) plane. It is not clear why cobalt should be deposited differently from nickel, although it may be noted that the lattice spacings of cobalt and copper are closer than those of nickel and copper. Let us consider a small projection of this nature shown in plan in figure 5, in which the planes *ABCD*, *AFED* are those denoted by *AB*, *CD* in figure 1. It is clear that in azimuth (*a*) only two sets of octahedral layers will be effective, viz. those on *AB* and *AF*, while in azimuth (*b*) there will be four effective octahedral layers, those on *AF*, *AB*, *AFED* and *ABCD*. This accounts for the splitting of the spots which was observed. The production of thin layers may again be attributed to twinning, for in some plates taken in azimuth (*a*) the lines and additional spots obtained with nickel were seen faintly towards the outside of the pattern. Usually, however, they will be obstructed in some way by layers on *AF*, *AB*, *CD* and *DE*.

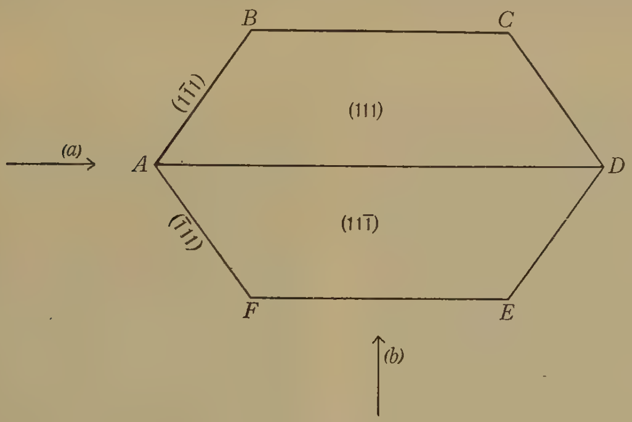

Figure 5.

§ 10. DISCUSSION OF RESULTS

The experiments indicate that metals with a cubic structure may be oriented as single crystals when deposited on the etched copper crystal. The current-density of deposition must not, however, exceed a certain value, otherwise only polycrystalline metal is obtained. This limiting value depends on the metal deposited. Thus copper deposited on the copper crystal at 0·3 mA./cm.^{2} gave a single-crystal pattern, but nickel deposited at this current-density was polycrystalline. Even at very low current-densities, such as 15 μA./cm.^{2}, silver deposits showed some rings due to polycrystalline metal. Hence the closer the agreement between the lattice constants of the deposit and the base, the higher is the limit of current-density for orientation.

Zinc and cadmium, which form close-packed hexagonal lattices but have not the theoretical axial ratio for perfectly close packing, do not appear to be oriented on the copper crystal, at least under the conditions used here.

The metals nickel and cobalt have lattice constants very close to that of copper and it is not surprising that thin layers of them should be deposited exactly like the copper crystal base and with the lattice constant of copper.

The silver deposits differ from those of nickel and cobalt in that the silver has its usual lattice dimensions. Thus the silver atoms cannot be considered as placed one by one immediately above the atoms of the copper base. Nevertheless the *angle* between two intersecting lattice planes of the silver lattice will be exactly the same as the angle between the two corresponding planes of copper. A projection on the surface of the copper crystal may be regarded as bounded by (111) planes, and to a lesser extent by (110) planes and by a few others including (100) planes(10). This is verified to some extent by examination of the etched crystal using Bridgman's sphere method(11). If, now, silver atoms are first placed along the edge between (111) and (110) copper planes and then the silver grows over these two copper planes from the edge considered, orientation of the silver as a single crystal will result. The orientation is not uniquely determined since this kind of growth might, for example, give rise to a (111) silver plane on (111) copper or a (111) silver plane on (110) copper. The similarity of arrangement of atoms in the (111) planes of silver and copper may be expected to have some slight effect also in producing orientation and this will produce the observed orientation of the silver on the copper crystal. Other explanations of the manner of deposition might be given, for example, in terms of growing-places. It is only desired here to record the two factors which could determine the orientation: (1) angular fit between a pair of lattice planes in the deposit and a pair of planes of the base; and (2) similar arrangement of atoms in contacting planes.

The orientation of chromium can be considered from the above point of view. Referring to figure 4, it may be shown that the (111) copper plane *GAB* is intersected at right angles along the line *AJ* by a (110) copper plane and by another (110) along *GH*. Again the (110) chromium plane *CDNP* is intersected at right angles along the line *KD* by a (111) chromium plane, where *K* is the mid-point

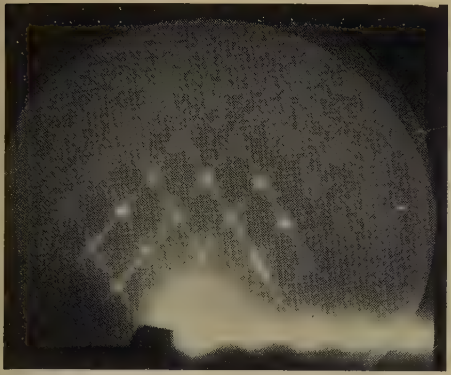

Figure 6.

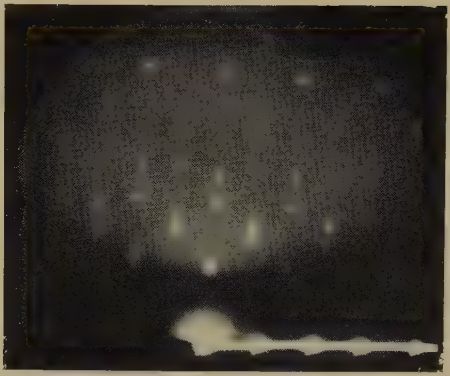

Figure 7.

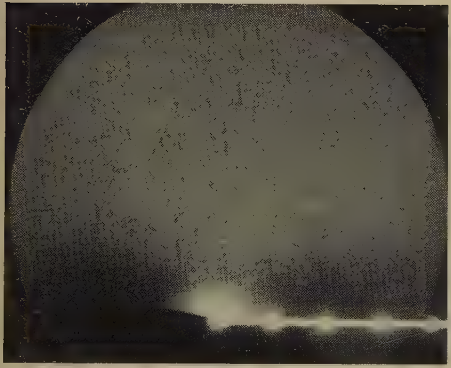

Figure 8.

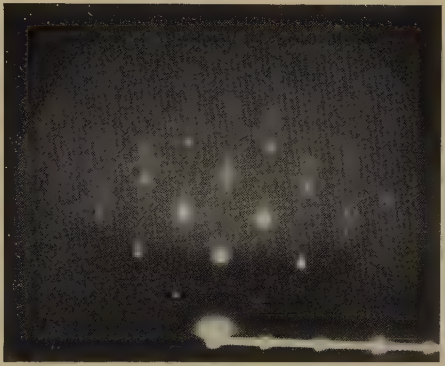

Figure 9.

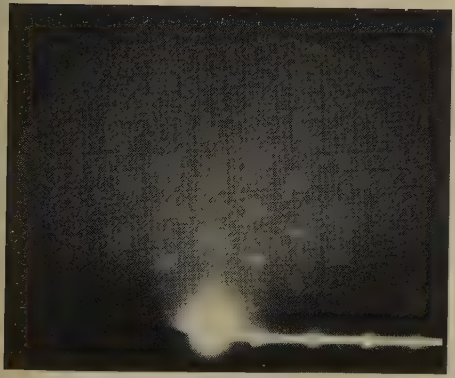

Figure 10.

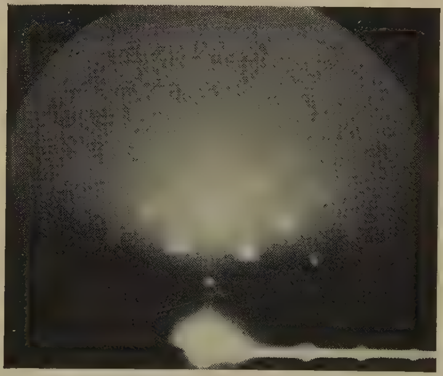

Figure 11.

of *CN*. Similarly, *EMFQ* is intersected at right angles by a (111) chromium plane along *ML*. The figure shows that *KD* is approximately parallel to *AJ*, and *ML* approximately parallel to *GH*. Now the positions of the chromium planes shown in figure 4 can only be regarded as correct to a few degrees because any etched crystal will continue to give the same diffraction pattern when it is turned slightly in azimuth from a given important azimuthal position. Thus there is a strong probability of an exact fit in angle between the chromium (110) and (111) planes and the copper (111) and (110) planes. The copper (111) planes are most extensive and the similarity of arrangement of the atoms in the (111) copper and the (110) chromium planes may decide the orientation observed.

§ 11. ACKNOWLEDGMENTS

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537·11

THE MASS OF A CONVECTED FIELD AND EINSTEIN'S MASS-ENERGY LAW

By Professor W. WILSON, F.R.S.

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ABSTRACT. Certain discrepancies between the results of the usual mode of calculating the mass (more particularly the electromagnetic mass) of a charged conductor and Einstein's mass-energy law are discussed and explained.

Einstein's law is contained in the now familiar statement

$$Energy = mass \times c^2 \qquad \text{......(1),}$$

in which c is the velocity of electromagnetic waves in empty space. This statement simply identifies mass and energy. Indeed a trivial change in the definition of energy as something which is measured by work done would enable us to write Einstein's law in the form

$$Energy = mass \qquad \text{......(2).}$$

I am only concerned with cases where a velocity of transport, $\mathbf{v}$, can be assigned to the energy, and the purpose of this communication is to discuss, and to suggest an explanation for, certain discrepancies between the results of the usual mode of calculating the mass—more particularly the electromagnetic mass—of a charged conductor and Einstein's mass-energy law. The electromagnetic contribution m to the mass of a charged spherical conductor which is moving slowly through empty space is usually taken to be given by

$$m = 2e^2/3c^2R \qquad \text{......(3),}$$

where e is the charge in ordinary electrostatic units and R is the radius of the sphere. A very simple calculation convinces us that the energy of the electrical field associated with the charge is

$$e^2/2R \qquad \text{......(4),}$$

and Einstein's law obviously requires that the associated mass m shall be given by

$$m = e^2/2c^2R \qquad \text{......(5).}$$

The expression (3) therefore makes the mass 4/3 times that required by Einstein's law.

When we carry out the calculation by applying the special theory of relativity we get for the electromagnetic contribution to the mass of the charged sphere the expression

$$2\gamma e^2/3c^2R \qquad \text{......(6)}$$

n ordinary electrostatic units, where γ is the factor

$$(1-v^2/c^2)^{-\frac{1}{2}} \qquad \text{......(7)},$$

provided we carry out the calculation in what I believe is the usual way, namely by calculating the total electromagnetic momentum and assuming the momentum per unit volume to be

$$\mathbf{p}/c^2 \qquad \text{......(8)},$$

where $\mathbf{p}$ is Poynting's vector.

The theory of relativity however enables us to carry out an analogous calculation for the rest of the mass and this yields the expression

$$\gamma\,\{E'/c^2-e^2/6c^2R\} \qquad \text{......(9)},$$

where E' means the energy of the sphere, exclusive of the electromagnetic part, when at rest. The second term in equation (9) has its origin in the elastic tension due to the surrounding field.

When we add together equations (6) and (9) to get the *total* mass of the charged spherical conductor we find it to be

$$\gamma\,(2e^2/3c^2R-e^2/6c^2R+E'/c^2),$$

or

$$\gamma\,(e^2/2c^2R+E'/c^2),$$

which may be written

$$\gamma E/c^2 \qquad \text{......(10)},$$

where E means the total energy, both electromagnetic and non-electromagnetic, of the sphere when at rest; so that the calculation of the *total* mass yields a result which is in conformity with Einstein's mass-energy law and the law expressing the dependence of mass on velocity.

The discrepancy, which only appears when we deal with the electromagnetic field alone or with the stress-tensor field within the conductor alone, or more generally when the calculation is extended over some limited portion of the region in which the energy is located, is intimately bound up, as we shall see, with the character of Poynting's vector and its analogue in an elastic stress-momentum field. It is well known that Poynting's vector cannot in general be identified with the vector which expresses the energy passing through the unit area per unit time. All that can be said about Poynting's vector, in general, is that its integral over a closed surface correctly expresses the rate at which energy flows from within outwards and it may be replaced in Poynting's theorem by any one of the infinite number of vectors that have the same divergence. In the case of the charged conductor and its convected field, for example, Poynting's vector has not even the same direction everywhere as that in which the energy is travelling and it actually vanishes in some places where there is a very appreciable transport of energy.

Without entering into the details of a calculation which is sufficiently well known it will be helpful to indicate how it comes about that the momentum $\mathbf{M}$ per unit volume in an electromagnetic field in empty space is commonly identified with $\mathbf{p}/c^2$. The x component f_x of the force per unit volume, i.e. the force on the charge in the unit volume, may be (quite correctly) expressed in the form

$$f_x=\frac{\partial t_x{}^x}{\partial x}+\frac{\partial t_x{}^y}{\partial y}+\frac{\partial t_x{}^z}{\partial z}+\frac{\partial t_x{}^w}{\partial w} \qquad \text{......(11)},$$

where x, y and z are rectangular co-ordinates, $w = \surd(-1)\, ct = ict$, t being the ti and $t_x^x, t_x^y, t_x^z, t_x^w$ are components of the *stress-momentum* tensor. In fact t_x^x, t_x^y, a t_x^z are components of the familiar Maxwell stress tensor. The fourth term in (1 may be written

$$-\frac{\partial}{\partial t}\left(-\frac{t_x^w}{ic}\right) \qquad \text{......(12),}$$

so that it is perhaps natural—but not necessarily correct, since we may add t_x^w/ic any function of x, y and z without affecting the partial differential quotie (12)—to identify the x component M_x of the momentum per unit volume wi $-t_x^w/ic$, i.e.

$$M_x = -t_x^w/ic \qquad \text{......(13).}$$

We have expressions like (11) for f_y and f_z and a fourth equation

$$f_w = \frac{\partial t_w^x}{\partial x} + \frac{\partial t_w^y}{\partial y} + \frac{\partial t_w^z}{\partial z} + \frac{\partial t_w^w}{\partial w} \qquad \text{......(14).}$$

This last equation is simply Poynting's theorem. In fact $-icf_w$ is equal to the rate which work is done on the charge per unit volume at the expense of the field energ and hence, if

$$p_x = ict_w^x \qquad \text{......(15),}$$

p_x is the x component of Poynting's vector. The tensor **t** is symmetrical, i.e.

$$t_x^w = t_w^x,$$

so that we get from (13) and (15)

$$-icM_x = p_x/ic,$$

or

$$M_x = p_x/c^2 \qquad \text{......(16).}$$

Poynting's vector **p** is, of course, in the units used in this paper (that is, ordina electrostatic units for electrical quantities and ordinary electromagnetic units f magnetic quantities) expressed by

$$p = \frac{c}{4\pi}\, \mathbf{E} \times \mathbf{H} \qquad \text{......(17),}$$

where **E** is the electric field-intensity and **H** the magnetic field-intensity, and t symbol × indicates a vector product. The momentum, **M**, per unit volume of t electromagnetic field, as given by (16), may therefore be expressed by

$$\mathbf{M} = \mathbf{E} \times \mathbf{H}/4\pi c \qquad \text{......(18).}$$

The calculation of **E** and **H** in equation (18) for the case of a charged sphere easily effected by using the Lorentz transformation. We start with co-ordinat x', y', z' in which the sphere of radius R is at rest. The electric field-intensity at a point distant r from the centre is

$$\mathbf{E}' = e/r^2,$$

while the magnetic field-intensity **H**′ is zero. We then transform to axes x, y, z whic are in motion in the common x' or x direction with the constant velocity **v**. We th find for M_x, the x component of the momentum per unit volume, at a point in t electromagnetic field the expression

$$M_x = \gamma^2 \mathbf{v}\, e^2 \sin^2\theta/4\pi c^2 r^4 \qquad \text{......(19),}$$

where r is the radial distance of the point from the centre of the sphere, measured in the co-ordinates in which the sphere is at rest, and θ is the angle between the radial line and the x' axis. We multiply this by the volume element

$$r^2 dr \sin\theta \, d\theta \, d\phi/\gamma,$$

and integrate over the whole electromagnetic field. The division by γ must be made because r, θ and ϕ are polar co-ordinates in the system in which the sphere is at rest. We thus get for the total momentum due to the electromagnetic field the expression

$$\gamma \{2e^2/3c^2R\} \, \mathbf{v} \qquad \text{......(20).}$$

The calculation of the momentum of the interior of the charged sphere is very similar. The stress-momentum tensor, referred to co-ordinates x', y', z', w' in which the sphere is at rest, has only the four following components which do not vanish:

$$\left.\begin{aligned} & t'^{x}_{x} = t'^{y}_{y} = t'^{z}_{z} = e^2/8\pi R^4 \\ \text{and} \qquad & t'^{w}_{w} = U', \text{ the energy per unit volume} \end{aligned}\right\} \qquad \text{......(21).}$$

On applying the appropriate equations of transformation to obtain the components of this tensor in the co-ordinate system in which the charged body is in motion with the velocity $\mathbf{v}$ in the x direction, we find

$$t_x^{w} = \frac{\gamma^2 v}{ic} \{t'^{w}_{w} - t'^{x}_{x}\}$$

or

$$t_x^{w} = \frac{\gamma^2 v}{ic} \{U' - e^2/8\pi R^4\},$$

and thus obtain for the x component of the momentum per unit volume

$$M_x = -t_x^{w}/ic = \frac{\gamma^2 v}{c^2} \{U' - e^2/8\pi R^4\},$$

and hence for the whole of the interior momentum, on multiplying by the volume $4\pi R^3/3\gamma$,

$$\gamma \{E' - e^2/6R\} \, \mathbf{v} \qquad \text{......(22).}$$

The fact that the calculations outlined above yield a result for the *total* mass and momentum which accords with Einstein's law, while they yield results for the mass and momentum of some *part* of the field which are generally in conflict with Einstein's law, can be explained in the following way.

If U be the energy per unit volume at *any* point in the field (whether in the electromagnetic field outside the charged conductor or in the elastic stress-tensor field within it) the associated mass is undoubtedly U/c^2, so that

$$\rho' = U/c^2 \qquad \text{......(23),}$$

where ρ' means mass per unit volume. The momentum per unit volume will be expressed by

$$\mathbf{M}' = U\mathbf{v}/c^2 \qquad \text{......(24).}$$

This, it should be noticed, is a correct expression for the momentum per unit volume and differs from that expressed by equation (18), for example, since at a point in the electromagnetic field equation (24) is equivalent to

$$\mathbf{M}' = (\mathbf{E}^2 + \mathbf{H}^2)\,\mathbf{v}/8\pi c^2.$$

The correct expression for the energy-transport vector is clearly

$$\mathbf{p}' = U\mathbf{v} \qquad \text{......(25)},$$

so that

$$\mathbf{M}' = \mathbf{p}'/c^2 \qquad \text{......(26)}.$$

If now we base the calculation of mass on equation (23) and the following equations we are bound to get correct results whether we deal with the whole or merely with a part of the field. The calculation of the total mass might be effected in the following way. We imagine a closed surface which includes a volume so large that all the energy—or all except an infinitesimal fraction—is within it at some instant t, and that all the energy has passed out of it during an interval of time τ, in consequence of the convection with the velocity $\mathbf{v}$. The total mass will then be expressed by

$$\text{Mass} = \int_t^{t+\tau} dt \iint \mathbf{M}' \,.\, \mathbf{dS} \qquad \text{......(27)},$$

where $\mathbf{dS}$ is a surface element and also a vector which is directed outwards and $\mathbf{M}' \,.\, \mathbf{dS}$ is a scalar product. The double symbol $\iint$ represents an integration over the whole of the closed surface. Finally, on making use of equation (26) we get

$$\text{Mass} = \frac{1}{c^2}\int_t^{t+\tau} dt \iint \mathbf{p}' \,.\, \mathbf{dS} \qquad \text{......(28)}.$$

If now in this equation we were to replace $\mathbf{p}'$, which is the true energy-transport vector, by Poynting's vector $\mathbf{p}$ (or its analogue in the elastic stress-tensor field) we should get a correct result, that is a result in agreement with equation (10) for the total mass, as we shall show. The difference between the two modes of calculation is due to using the faulty expression (16) for momentum-density in one case and the correct one (26) in the other. Now it is a property of Poynting's vector (and of its analogue) that the surface integral $\iint \mathbf{p} \,.\, \mathbf{dS}$ correctly expresses the rate of flow of energy through the closed surface from within outwards, notwithstanding the fact that $\mathbf{p}$ does not in general express the transport of energy through the unit area per unit time. Therefore

$$\iint \mathbf{p}' \,.\, \mathbf{dS} = \iint \mathbf{p} \,.\, \mathbf{dS},$$

and we have an explanation of the fact that we get a correct expression for the total mass while using a faulty expression for the momentum-density.

538.222:546.66

THE PARAMAGNETISM OF THE RARE-EARTH SULPHATES AT LOW TEMPERATURES

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ABSTRACT. The magnetic susceptibilities of powdered specimens of the octahydrated sulphates of ytterbium, dysprosium and erbium have been measured from room temperature down to 14° K. The results are discussed in terms of the crystalline-field theory of Penney and Schlapp. Measurements on $Nd_2(SO_4)_3 . 8H_2O$ support the observations of Gorter and de Haas as against those of Selwood.

§ 1. INTRODUCTION

The measurements made by Gorter and de Haas⁽¹⁾ in the temperature range 290° to 14° K. of the magnetic susceptibilities of the octahydrated salts of praseodymium and neodymium showed that those salts obey the law

$$\chi(T+\Delta)=\text{a constant}$$

at the higher temperatures. Deviations however set in as the temperature falls, the susceptibility of the praseodymium salt increasing *less* rapidly with decrease in temperature and becoming almost independent of T below 20° K., while that of the neodymium salt increases more rapidly with decrease in T than is given by the above formula. These strikingly different behaviours have been shown by Penney and Schlapp⁽²⁾ to be explicable on the same theoretical basis. The paramagnetic ion is assumed to be situated in an inhomogeneous electrostatic field of appropriate symmetry and strength. Each of the energy levels of the free ion is split in this crystalline field into a number of levels, the separations between which are small compared with the distances between the levels of the free ion in the case of the rare-earth salts.

The variation with temperature of the population of these sub-levels then gives rise to the deviations from the Curie law, $\chi T=$ a constant, observed with these salts. The different behaviour of praseodymium and neodymium salts is due to the difference in the effect of the same crystalline field on ions containing an even and an odd number of electrons respectively.

By a suitable choice of the strength of a field of cubic symmetry, Penney and Schlapp were able to reproduce the experimental results in a very satisfactory way and to deduce the situations of the energy levels of the paramagnetic ions in the crystals.

Now since all the rare earths, with the possible exception of cerium, give octa hydrated sulphates and since the crystalline fields of all these salts may be expecte to be very similar in strength and symmetry, it would appear to be of considerabl interest to extend the measurements to as many of the other rare earths as possible The applicability of the crystalline-field theory could be further tested and in th event of its success the energy levels of the various paramagnetic ions in the crystal could be determined. With this end in view a series of measurements has bee commenced in this laboratory on material of very high and accurately known purity over the temperature range 290–14° K.

The present paper deals with the observations on the sulphates of ytterbium dysprosium and erbium. In addition, the susceptibility of neodymium sulphate ha been investigated with the object of deciding whether the results of Gorter an de Haas or the more recent ones of Selwood(3) are the more nearly correct.

§ 2. EXPERIMENTAL RESULTS

The susceptibilities of powdered specimens of the rare-earth sulphates wer determined over the range of temperature 290–14° K. by means of the Sucksmit magnetic balance adapted for use at low temperatures as described in a previou paper(4). The low temperatures were obtained with the aid of baths of liqui ethylene, oxygen, nitrogen and hydrogen boiling under suitable pressures, together with solid carbon dioxide and acetone. The finely powdered specimens wer enclosed in small sealed spherical phials of pyrex glass.

Ytterbium sulphate, $Yb_2(SO_4)_3.8H_2O$. This was prepared from a sample of ytterbium oxide (Lab. No. 8218) supplied by Messrs Adam Hilger. The report of a spectroscopic analysis accompanying the specimen indicated that slight traces of calcium and sodium were present, but barium, cerium, erbium, europium, gadolinium, lanthanum, magnesium, manganese, scandium, strontium, terbium and yttrium were definitely absent.*

The reciprocals of the molecular susceptibilities, corrected for diamagnetism,† are plotted in figure 1, curve I.

It will be seen that ytterbium sulphate obeys the law $\chi(T+\Delta)=$ a constant, with Δ equal to $+42$ down to about 60° K., but that at lower temperatures the susceptibility is greater than is given by the above expression.

This behaviour is to be expected for a magnetically dilute salt containing a rare earth ion with an odd number of electrons.

Dysprosium sulphate, $Dy_2(SO_4)_3.8H_2O$. The specimen used was prepared from the oxide (Lab. No. 6402) supplied by Messrs Adam Hilger. Spectroscopic analysis showed that the sample contained a trace of magnesium and perhaps slight traces of calcium and gadolinium. Cerium, lanthanum, neodymium, samarium and yttrium were absent and praseodymium "probably absent". The corrected reciprocals of the observed susceptibilities are plotted in figure 2, curve I.

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* When an element is stated to be "absent", the substance under examination does not contain as much as 0·01 per cent of it, except that for praseodymium, the corresponding figure is 0·1 per cent.

† The following values of the gram-molecular susceptibilities have been used in calculating the correction for diamagnetism: $SO_4=-33{\cdot}4\times10^{-6}$, $H_2O=-13{\cdot}0\times10^{-6}$. No correction has been applied for the diamagnetism of the rare-earth ion in view of the uncertainty of the value to be taken. The correction still to be applied may therefore amount to ½ per cent for Yb^{+++} at room temperature but is negligible for the other ions.

Dysprosium sulphate thus follows the law $\chi\,(T+\Delta)=$ a constant, with Δ equal to about 1·5 down to the lowest temperature investigated.

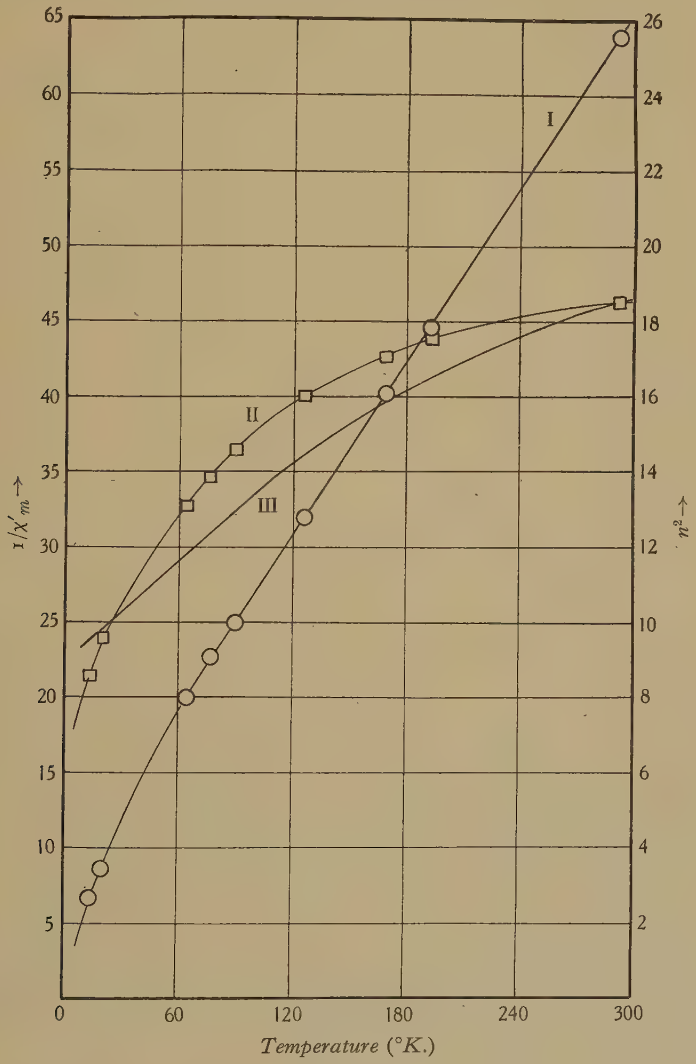

Figure 1.

Erbium sulphate, $Er_2(SO_4)_3.8H_2O$. The specimen was prepared from oxide (Lab. No. 10374) supplied by Messrs Adam Hilger. They report that a spectroscopic examination showed the doubtful presence of a trace of yttrium but no other impurities. The corrected reciprocals of the observed susceptibilities are plotted in figure 2, curve II.

These results fit the formula $\chi(T+6)=$ a constant, down to the lowest temperature investigated.

Neodymium sulphate, $Nd_2(SO_4)_3.8H_2O$. The specimen used was prepared from the oxide (Lab. No. 6783) supplied by Messrs Adam Hilger. The report of a spectroscopic analysis of the sample showed that it contained 0·1 per cent of gadolinium, 0·03 per cent of lanthanum, and 0·1 per cent of samarium, together with a trace of magnesium and a slight trace of calcium. The data for the susceptibility were corrected in accordance with this analysis. As the susceptibilities obtained agreed within their estimated accuracy with those of Gorter and de Haas it is not thought necessary to reproduce them here. It may be mentioned that Selwood's results for this salt can all be made to agree with those of the last-mentioned workers by multiplying throughout by a factor of about 0·9. It would thus seem that his results are affected by some error of calibration and that in view of their confirmation by the present work the susceptibility data given by Gorter and de Haas for $Nd_2(SO_4)_3.8H_2O$ may be regarded as correct.

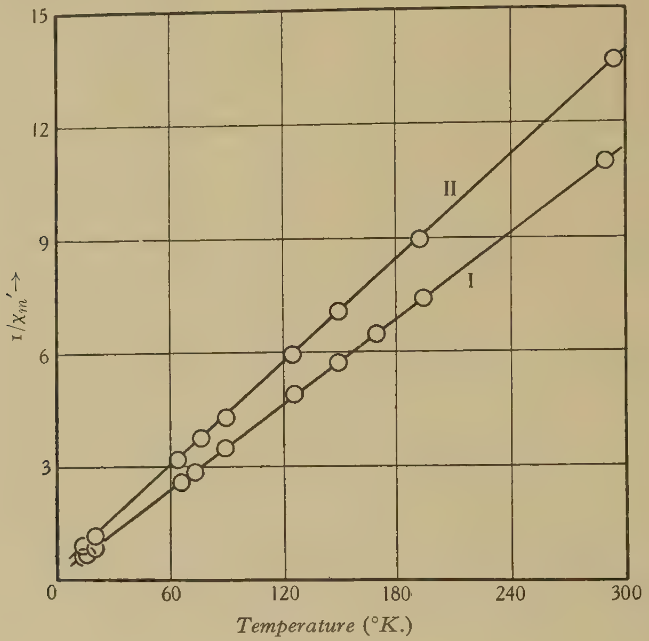

Figure 2.

§ 3. DISCUSSION OF THE RESULTS

In comparing the experimental results with the predictions of the crystalline-field theory, the susceptibilities are calculated by means of the general expression (1)

$$\chi_m = -\frac{N}{H}\Sigma\frac{\partial W}{\partial H}e^{-W/kT} \div \Sigma e^{-W/kT} \qquad \text{......(1)},$$

in which χ_m is the molecular susceptibility, N the Avogadro number, and W the energies of the various levels in the presence of the magnetic field. The summation is to be made over all the levels which contribute appreciably to the magnetization. In the case of the magnetically dilute compounds of the rare earths, the levels in question except for europium and samarium will be the ones into which the lowest component of the fundamental multiplet (the ground state) is split by the crystalline field.

The energies W have then to be calculated assuming some particular properties of the crystalline field in respect of symmetry. The over-all splitting of the levels depends on the strength of this crystalline field and their number on its type of symmetry.

Ytterbium. In the presence of a crystalline field of cubic symmetry, the lowest state of the Yb^{+++} ion ($J=7/2$) is split into two two-fold degenerate levels and one four-fold degenerate level. When a magnetic field is applied, these levels split into the following eight levels⁽⁵⁾:

$$\begin{aligned} W_1 &= -14a + 1{\cdot}167\,G - 0{\cdot}3240\,G^2/a, \\ W_2 &= -2a + 1{\cdot}833\,G + 0{\cdot}3240\,G^2/a, \\ W_3 &= -2a + 0{\cdot}500\,G - 0{\cdot}1500\,G^2/a, \\ W_4 &= 18a - 1{\cdot}500\,G + 0{\cdot}1500\,G^2/a, \end{aligned}$$

and four more obtained by changing the sign of G. In the above expressions $a=12pD$, where D is a constant expressing strength of the cubic field and p involves an integral of a radial wave function taken over the whole ion and is nearly the same for all the rare-earth ions, $G=g\beta H$, g being the Landé factor, β the Bohr magneton, and H the strength of the applied magnetic field.

Calculations have been made with the aid of the above expressions, and the curve for n^2 (where n is the effective Bohr magneton number $=3\chi'_m kT/N\beta^2$) which passes through the experimental value at room temperature is plotted in figure 1, curve III. It will be seen that the assumption of a crystalline field having cubic symmetry does not reproduce the experimental results (figure 1, curve II) at all accurately. It remains to test whether a field of lower symmetry will give satisfactory agreement or whether other factors have to be taken into account in the explanation.

Dysprosium and erbium. The ground state for the ions of both these elements is split by a crystalline field of cubic symmetry into two two-fold degenerate levels and three four-fold degenerate levels ($J=15/2$). The calculation of the expressions for the levels in the presence of a magnetic field is, however, very complicated for so high a value of J and has not yet been carried out. If, however, it is permissible to estimate the width of the over-all splitting due to the crystalline field in the case in which $J=15/2$ from the known results for those in which $J=7/2$, 4 and 9/2* it is seen that this over-all splitting for dysprosium and erbium must be at least ten times as great as that for neodymium with the same strength of the electric field. Thus although the positions of the separate levels are unknown, the separation between the lowest and the next highest level will, in the absence of a magnetic field, be 2000 $cm.^{-1}$ or more for the octahydrated sulphates of these two elements. It is thus clear that any levels but the lowest will be practically unoccupied even at room temperature. The magnetic behaviour of these salts will therefore deviate but little from Curie's law in agreement with the experimental observations.

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* 384, 296 and 1823 A. respectively for a field of cubic symmetry such that $A=pD$.

Further consideration of the results shows that this cannot be the correct explanation, for the magneton number deduced from the susceptibilities would be quite different from the Hund value for the free ion, whereas the experimental value for the effective magneton number is almost equal to the Hund value at any temperature above about 60° K. To account for this result and for the small deviation from Curie's law it is necessary to assume that the over-all splitting of the ground state by the crystalline field in these salts is very small, and indeed not more than about 40 $cm.^{-1}$, as against the observed value 834 $cm.^{-1}$ for the corresponding salt of neodymium.

This result is surprising since $Er_2(SO_4)_3.8H_2O$, and presumably also $Dy_2(SO_4)_3.8H_2O$, is isomorphous with $Nd_2(SO_4)_3.8H_2O$ and the molecular volumes of these salts do not differ greatly. It would therefore be expected that the crystalline fields in all three of the salts would be very similar as regards strength and symmetry. It appears, however, that, unless there is some at present unsuspected factor which results in the states of high *J*-value being much less affected by a cubic crystalline field than those of lower *J*, the strength of the field in $Dy_2(SO_4)_3.8H_2O$ and $Er_2(SO_4)_3.8H_2O$ is very small.

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535.8:612.84

VISION IN OPTICAL INSTRUMENTS*

By CHARLES FABRY

The Thomas Young Oration, delivered December 6, 1935

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§ 1. THOMAS YOUNG

To me it is a great honour to have been invited to give this lecture in honour of Thomas Young.

You will not expect from me a summary of the extremely extensive work of Thomas Young. I should like, however, to remind you of the admiration felt for him by French physicists, even during his own lifetime. He was probably more fully appreciated in France than in his own country. Young had many friends in France, he came several times to Paris, and certain of his French friends went to London for the special purpose of conferring with him, particularly on the theory of light, which was then receiving much attention in France. At the time of Young's death, Arago was the Secretary of the Académie des Sciences, of which Young was of course a foreign member. Now, our Academy holds an annual formal meeting, at which Arago was accustomed to read an "éloge" on some recently deceased scientist whom he had known personally. Naturally, the man to whom he rendered this homage was generally French, and I have only found three exceptions to this rule: James Watt, Alessandro Volta and Thomas Young, and the juxtaposition of these three names shows how Thomas Young was admired.

Young lived in a very brilliant period of French science, with men like Laplace, Lagrange, Fourier, Monge, Ampère, Fresnel, Poisson, Arago and others. The complete understanding of Thomas Young's work in French scientific circles is very remarkable, because of the great difference in their mental outlook. The characteristic feature of French science at this time was its very strong mathematical bias; Young was not ignorant of mathematics (there was probably nothing in which he was ignorant), but mathematics was not his natural language. Laplace expressed this peculiarity by saying that in the work of Thomas Young there were more general surveys than accurate demonstrations. Perhaps in Laplace's mind this opinion implied a certain criticism of Young; we should add that Young's general arguments were those of a great genius, and that the two types of mind, that which eads to general conclusions and that which ends up in a mathematical demonstration, are both necessary to the progress of science.

* Translated by Mr J. H. Awbery.

§ 2. THE PROBLEMS OF VISION

I shall speak of vision in optical instruments, or of the eye considered as a part of every instrument which assists vision. The problems to be solved are the following: what can we *see* in a given optical instrument, and as a correlative question, how must an instrument be constructed to *see* a certain thing? First of all it is necessary that the details which we wish to see should be truly separated by the instrument; but in general this is not sufficient.

Geometrical optics indicates no limit to the resolution in a perfect instrument. This idea is curiously expressed by Descartes in his Dioptrics, published almost exactly three centuries ago, at a time not very distant from the first astronomical discoveries made by Galileo with the telescope. Applying the exact law of refraction to the theory of the telescope for the first time, Descartes discovered what is now called spherical aberration in objectives, and expressed the opinion that this aberration was the sole cause which limited the resolving power of the telescope. He sought therefore what form must be given to the surfaces in order to obtain an exactly stigmatic image, and showed that this result would be reached by means of a lens with one plane face and one in the form of a convex hyperboloid—an easy problem for a present-day student, but difficult enough half a century before Newton. Descartes added that if such a lens were to be made it would enable entirely new things to be seen, such as the inhabitants of the moon. Descartes was so sure of his results that he designed a machine for shaping the hyperbolic surface and spent a certain amount of money, including that of his friends, in building it. We have never heard that he was repaid by seeing the inhabitants of the moon.

Much later, the theory of diffraction permitted the calculation of the effect of a perfect optical instrument, independently of the eye, following the general ideas of Young, the more penetrating theory of Fresnel, the complete calculations of Airy, and Foucault's experimental studies. This theory gives the form of the diffraction pattern in a perfect instrument when forming an image of a luminous point; from it is deduced the limiting separation for a set of two points, such as a double star. The result is as follows: a 5-in. objective can just separate two points with an angular distance of 1 sec., and this limit falls off inversely as the diameter of the objective.

Now it is quite evident that this criterion of resolution does not in general represent what can really be seen. For example, the star Sirius has a companion of the 8th magnitude at a distance of about 8 sec. from the main star. A 2-in. telescope should thus show the satellite easily; actually, I believe that a ten times greater diameter is necessary for seeing it.

Again, the theory of diffraction assumes that the instrument is geometrically perfect. In testing an instrument, it is common to use Foucault's test object, formed of equidistant black lines on a white background, the width of the black lines being equal to that of the transparent intervals. The theory of diffraction gives the limit of the angular interval that can be separated, and an instrument is regarded as good if its resolving power is equal to the theoretical power. Now experience shows that if the test object is well illuminated, practically all instruments, even the most ordinary, have the theoretical resolving power; nevertheless, the different instruments are far from being equally effective in use, and a simple glance at a landscape gives a more useful indication of the value of the instrument than does an examination by means of Foucault's test object.

On examining how a real object differs from the test object, we find two essential differences: (1) In a landscape, objects are seen which present only a feeble contrast both internally and to the background, whereas Foucault's test object shows complete contrast (black and white); (2) The brightness is not in general within the control of the observer, and may vary within extraordinarily wide limits (for example, from 1 to 10^9).

We must therefore commence by studying the capacity of the eye to grasp details under these various conditions. Moreover, in the majority of instruments, the pupil of the eye is restricted by the exit pupil of the instrument.

We are thus led to study the conditions of vision by the naked eye, introducing the three quantities which follow. (1) *Contrast*. The test object is composed of equal equidistant lines, but instead of presenting a complete contrast, these should exhibit simply a difference in brightness between the "light lines" and the "dark lines". If B and b are the brightnesses of these two parts, the contrast γ is defined as $\gamma=(B-b)/B$. The case of Foucault's object (black lines, $b=0$) corresponds to $\gamma=1$ (complete contrast). The other extreme case is $\gamma=0$ (complete absence of lines). (2) *Brightness*. The brightness of the test object is characterized by the value of B, the brightness of the lightest parts. A unit must be selected for this quantity. Brightness is luminous intensity per unit of area; we shall express it in candles per cm.², a unit to which M. Blondin has proposed to give the name of *stilb*; this name was recently approved by the International Commission on Illumination. It is rather too large a unit, but this is only of minor importance. To link this up with British units, we may consider a perfectly white object diffusing according to Lambert's law; if it receives illumination E foot-candles, then its brightness in stilbs is

B, b, γ

E

$$B=3{\cdot}43\times10^{-4}E.$$

Values of B greater than 0·01 stilb correspond to well-lighted objects, those less than 10^{-6} to feeble or very feeble illumination, whilst the limit of perception (below which a surface cannot be distinguished from perfect darkness) is about 10^{-10} stilb. (3) *Diameter of pupil utilized*. This will be expressed in millimetres and designated by ω. In an optical instrument this is, most usually, the diameter of the exit pupil. In experiments on the naked eye, it will be an artificial pupil consisting of a small circular aperture in a thin metal plate.

ω

When these three variables are fixed, we may seek the limit of separation,* defined as the least angular distance between the centres of two similar marks at

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* The expression "resolving-power" easily gives rise to confusion. This "power" is expressed as the least visible angle; the smaller the angle, the better is the resolution. When we say that the resolving-power is increased, it is difficult to know whether the instrument is better or worse. For this reason I shall speak of "limit of separation".

s which they can be distinguished as separate. It will be denoted by s and expressed in minutes of arc.*

The result of this study of the eye will be to determine a function s of three variables, such that

$$s=f(\gamma, B, \omega).$$

The experimental study of a function of three variables is always a long task. The present one has already given rise to numerous investigations, among which I would mention those of Luckiesh and Moss, and that of P. W. Cobb, Danjon, Dufay and Mlle Schwégler. Each of these researches covers only a part of the field of useful variation in γ, B and ω; in particular they do not extend sufficiently far into the region of low brightness and weak contrasts, which is the most interesting for certain applications of optical instruments. I shall refer particularly to the very complete and careful measurements carried out at the Institut d'Optique by M. A. Arnulf, with the co-operation of several workers at the same laboratory;† these measurements have not yet been published.

§ 3. CONSTRUCTION OF TEST OBJECT WITH VARIABLE CONTRAST AND BRIGHTNESS

The object employed is similar to that of Foucault, but with a greater or less contrast between the light lines and the darker ones. To obtain this result, the simple method of the revolving disk has been used. On a white carboard disk concentric black circles are traced, the width of the black bands being equal to the white portion left between two successive black bands. Each black circle extends over a part only of the circumference. When the disk is turned rapidly, only white and grey circles are seen; if the black circles occupy $1/n$ of the circumference, the contrast $\gamma=1/n$. In the case shown in figure 1, $\gamma=0{\cdot}5$. There is thus a series of disks, each corresponding to a given value of γ, from $\gamma=1$ to $\gamma=0{\cdot}006$. The diameter of the disk is 30 cm.; it is mounted on the shaft of an electric motor which turns it at the rate of 4000 r.p.m.; under these conditions, the surface of the disk is seen without any flickering. A black screen covers part of the disk, leaving a rectangular area visible, figure 1; it is this rectangle which serves as test object.

In order to vary the brightness, it is only necessary to vary the illumination of the disk. For high brightness, the disk is illuminated directly by means of an electric arc, and for less brightness by a tungsten strip lamp; for still less brightness, the arrangement shown in figure 2 is used; L is a tungsten strip lamp, which shines on a diffuser D provided with a variable diaphragm. In order to reduce the brightness further, a neutral filter of known transmission is put at E.‡ In each case, the brightness B (that of the light parts of the object) is directly measured by means of Jobin and Yvon's photometer, the measurements being taken on the white parts when the disk is stationary. For the smallest brightnesses, of which the direct measurement would be very uncertain, the measurement is made before inserting the filter, and then applying the accurately known transmission factor.

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* It would be more logical to express it in radians, but the minute as a unit of angle is more familiar.

† I tender my thanks to Mr Arnulf who has allowed me to make use of these results as well as of important theoretical suggestions before publishing them himself.

‡ The Institut d'Optique has an excellent collection of neutral filters, which is a gift of great value from Prof. Tscherning of Copenhagen. These filters are remarkably homogeneous and remarkably neutral, and their transmission factors, which vary from $0{\cdot}56$ to 10^{-10}, are very exactly known. Their use has contributed greatly to facilitate the measurements.

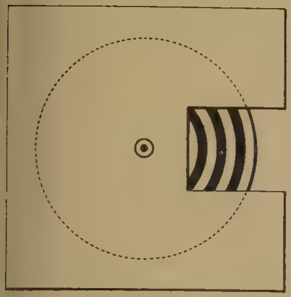

Figure 1.

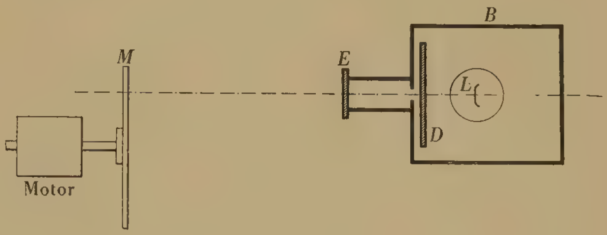

Figure 2.

To obtain various apertures ω of the pupil, a number of accurately circular holes are made in a thin metal sheet which the observer places in front of his eye. The diameters of these openings are measured by means of a comparator.

§ 4. PROCEDURE IN EXPERIMENTS ON VISION WITH THE NAKED EYE

Each disk gives a definite value of the contrast γ. After a disk has been inserted it is subjected to a definite illumination and therefore has a definite brightness, which is measured. The observer places a pupil of known diameter ω before his eye; he goes in front of the rotating disk, in complete darkness (after an adaptation period which is the longer the less the brilliance), and he finds the maximum distance at which he can still distinguish the marks; from this, the limit of separation s corresponding to the particular values of γ, B and ω is deduced.

The observer changes the pupil (which only means that he looks through a different hole in the metal plate) and resumes the observations, and so on for all the values of ω. The illumination, and consequently the brightness is then changed, and the observer goes through the same series again. Finally the rotating disk is changed, in order to alter γ, and the double series of measurements is repeated.

All the observers were youthful, and had good accommodation and normal vision. Certain observers who had an incurable tendency to regard the experiments as a sort of sporting contest, with the one who could see the marks at the greatest distance as the winner, had to be eliminated. The observations were very lengthy, owing to the necessity of varying three independent variables, especially the brightness, between very wide limits. The experiments are particularly fatiguing at very low brightnesses, where complete darkness and a long adaptation are essential.

§ 5. RESULTS

The results of the measurements are represented on a series of diagrams, each referring to a given value of the brightness. On each diagram, the pupil diameters ω are plotted as abscissae and the limits of separation s as ordinates, each curve referring to a given value of the contrast γ. Figures 3, 4 and 5 show examples of these diagrams for three different values of the brightness, one strong, one medium, and one low.

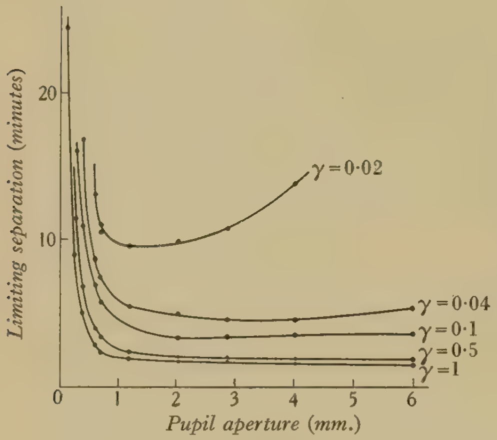

Figure 3. Brightness of the object, $0\cdot148$ candles/cm^2

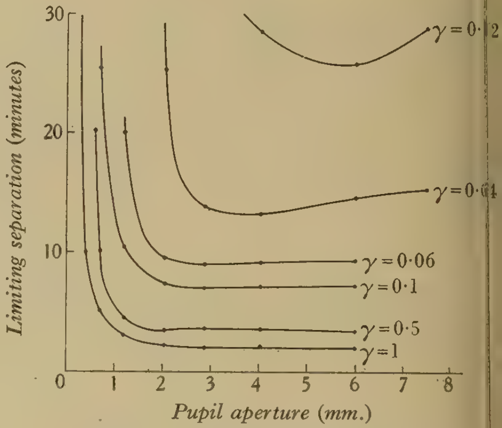

Figure 4. Brightness of the object, $1\cdot2\times10^{-4}$ candles/cm^2

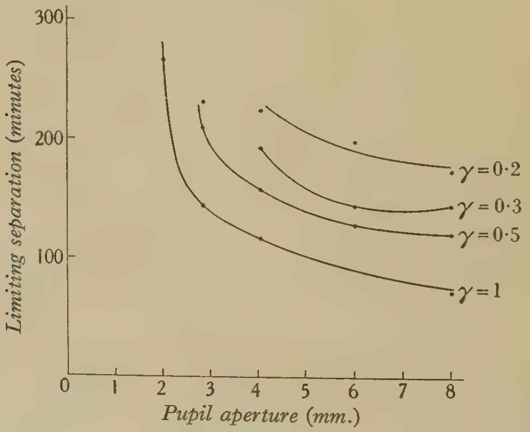

Figure 5. Brightness of the object, $0\cdot4\times10^{-8}$ candles/cm^2

Consider first a high brightness like that encountered in a well-lit landscape; the results are shown in figure 3, for which B is $0\cdot15$ stilb (i.e. equal to the brightness of a white diffuser under an illumination of 400 foot-candles). For very good contrast, we have the curve marked $\gamma=1$; the value of the limit of separation is practically constant for all sizes of the pupil greater than 1 mm.; this limit only increases as ω becomes very small, and it increases indefinitely as ω approaches zero. For slight contrasts the values of s become much greater, and the curve is altered in shape. The limit of separation passes through a minimum at a certain size of pupil; for example, at the very low contrast $\gamma = 0{\cdot}02$ the minimum of s corresponds approximately to $\omega = 1$ mm., and this minimum of the limit of separation is about 10′, ten times as large as for complete contrast.

If now we consider weaker and weaker brightnesses, down to the limit of perception which lies at about 10^{-10} stilb, we find that all the values of the limit of separation increase considerably, and at the same time the shapes of the curves are altered. Examples of these changes are seen in figures 5 and 6, which correspond to brightnesses of $1{\cdot}2 \times 10^{-4}$ and $0{\cdot}4 \times 10^{-8}$ stilb. The enormous values which the limit of separation can attain will be noticed; whilst values in the neighbourhood of 1′ are found with high brightness and good contrast, yet for low brightness the minimum of s can reach 258′ (i.e. more than 4°). This is why at night black objects can only be seen against the sky if their apparent diameters are considerable.

§ 6. COMPARISON WITH THE THEORY OF DIFFRACTION. SPECIFIC LIMIT OF SEPARATION

These results are in total disagreement with those predicted by the theory of diffraction for a perfect instrument. Moreover, that theory takes no account either of brightness or of contrast; it leads to a simple relation between s and ω, of the form $s\omega = \text{constant}$. The curve would be a hyperbola with the axes as asymptotes. This is approximately verified for a region containing extremely small pupil-sizes in the case of good contrast and high brightness, but not at all for the remainder of the curve.

Mr Arnulf considers the quantity σ equal to $s\omega$. It is convenient in the study of instruments, and he proposes to call it the *specific limit of separation*. This quantity would be a constant if diffraction alone were operative. A series of diagrams can be drawn for σ analogous to those for s. Each diagram refers to one value of the brightness; on each, the pupil diameter ω is taken as abscissa and the specific limit of separation σ (in millimetres × minutes of arc) as ordinate. If diffraction alone acted there would be a single diagram consisting of a horizontal line. Figures 6, 7 and 8 give examples of diagrams obtained for three values of the brightness, viz. $B = 0{\cdot}15$ (high brightness), $B = 1{\cdot}1 \times 10^{-5}$ (low) and $B = 0{\cdot}4 \times 10^{-8}$ (very low). σ

For high and medium brightnesses (e.g. $B > 10^{-4}$, which corresponds to a white body with an illumination of 0·3 foot-candles), the curve has a straight part, and then a minimum as ω diminishes, finally rising again for very small values of ω. The value $B = 10^{-5}$ is a transition region, a sort of twilight, where the curves are irregular and complicated; it is probably the region where red-sensitivity disappears. At very low brightnesses, as for example that of the night sky on a moonless night, and corresponding to nocturnal vision, the curves become regular again, but now have no minimum; σ decreases steadily as ω diminishes.

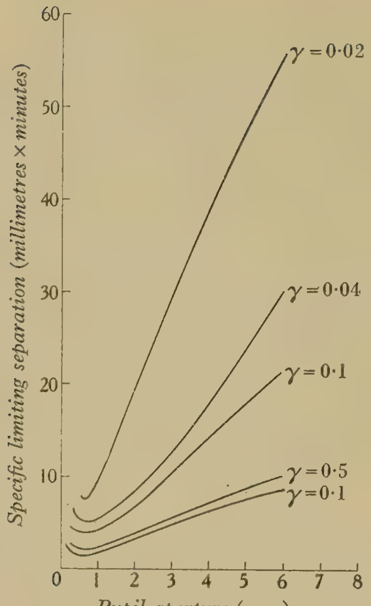

Figure 6. Brightness of the object, 0·15 candles/cm²

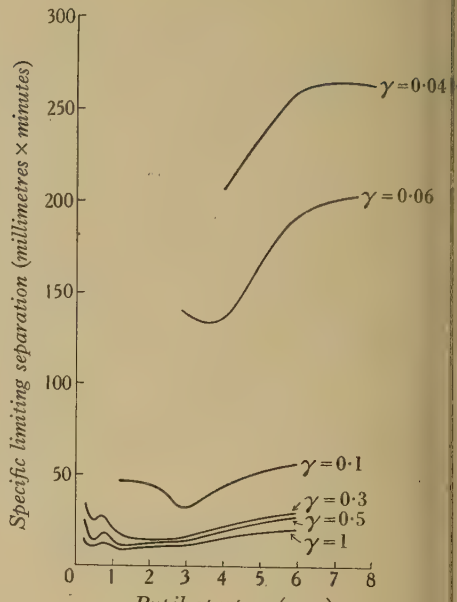

Figure 7. Brightness of the object, $1{\cdot}1 \times 10^{-5}$ candles/cm²

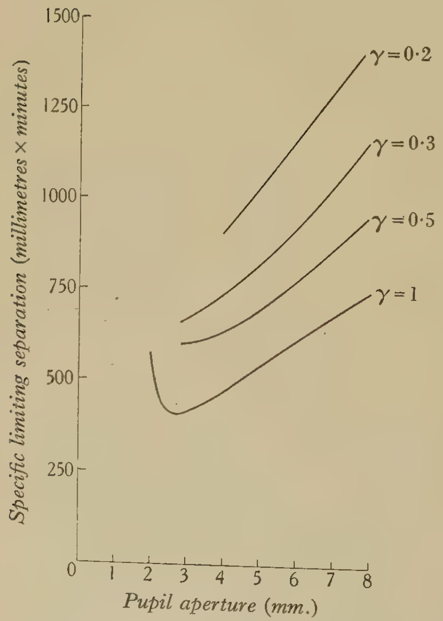

Figure 8. Brightness of the object, $0{\cdot}4 \times 10^{-8}$ candles/cm²

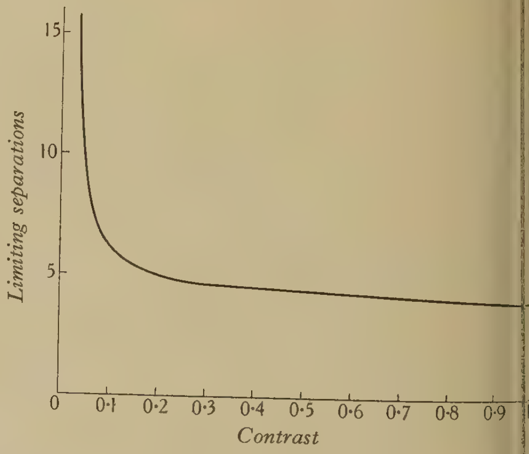

Figure 9.

This assemblage of diagrams (of which only a small part is reproduced here) gives complete information on the quantities s and σ as functions of the three variables γ, B and ω. From them all the curves which result from varying one or other of the three independent variables, the two others remaining constant, can be obtained, if desired. For example, figure 9 refers to a constant brightness $B=0{\cdot}01$ (good illumination) and a constant aperture $\omega=0{\cdot}54$; it gives the values of the limiting separation s as a function of the contrast γ. It will be seen that the limit increases as the contrast diminishes.

§ 7. CAUSES OF THE LIMITED RESOLVING-POWER OF THE EYE

What is the cause of the enormous disparity between the properties of the eye and the predictions of the theory of diffraction? Two causes may be acting, (1) the aberrations of the optical system of the eye and (2) the imperfect resolving-power of the retina. A similar set of circumstances occurs in the photography of distant objects, where the resolving-power is limited by the aberrations of the objective and by the imperfections of the plate (grain, thickness of the sensitized layer, diffusion of light in this layer). In the photographic case, the two kinds of imperfection can be studied independently; this is more difficult in the case of vision, because of the impossibility of studying the receptive properties of the retina apart from the optical system. An ingenious method was suggested by Mr Le Grand;* I will speak of it, although it lies outside my subject, because it is an application of a celebrated experiment by Thomas Young.

A system of interference fringes is produced on the retina by placing two parallel slits in front of the eye, and looking at a bright line. The aberrations of the optical system do not affect these fringes; their spacing can be altered by varying the distance between the slits, and the angular distance between consecutive fringes is in each case known. Again, the contrast can be varied by cutting down the light on one of the slits by means of a rotating sector; and the brightness is varied by altering the source of light. We have thus on the retina an exactly known test object; we can observe the disappearance of the fringes, due solely to the properties of the retina, as the slits are gradually separated, which gives the limit of separation of the retina alone. On the other hand, comparison with vision when the optical system takes part can be obtained by examining a set of interference fringes with no diaphragm over the eye, for example fringes from a Babinet's compensator, the spacing being easily varied by altering the distance of vision, and the contrast by variation of the polarizers.

I shall not speak of the results, since I wish to base my arguments on the facts of vision observed directly, and on their applications to optical instruments.

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* *C.R. Acad. Sci.*, Paris, **200**, 490 (1935).

§ 8. APPLICATION TO A PERFECT OPTICAL INSTRUMENT

I assume that the instrument examined is *perfect*, i.e. that it gives images exactly in accordance with the theory of diffraction, that its transmission coefficient is 100 per cent, and that it gives no stray light.

The theory of diffraction asserts that the instrument separates a certain angular distance between two points or lines; it is by no means certain, or even probable, that we shall see the two points or lines as separated.

We have to consider the object space and the image space. What we see has reference to the object space: I see a man on yonder mountain, an aeroplane in the sky, and so on; but the properties of the eye refer to the image space. The relations between the two are given by geometrical optics, and the diffraction system follows the same laws: we may think of the diffraction system in the object space, and the perfect instrument gives the geometrical image of this system in the image space. Finally, the image of a point is a small disk (if we neglect the diffraction rings, which are very faint) in a microscope, just as in a telescope. This disk behaves like a true object, and follows the laws of geometrical optics; the eye looks through an aperture which, usually, is the exit pupil of the instrument. Exceptionally, as in the Galilean telescope and many periscopes, it is the opening of the pupil of the eye itself.

Let us consider the case of a telescope. We have to consider the following
O quantities: Total diameter of the objective, O; effective diameter of the objective,
Ω, I, ω_0 Ω; exit pupil, I; total diameter of the pupil of the eye, ω_0; effective diameter of the
ω, M pupil of the eye, ω; magnification, M.

The laws of geometrical optics give

$$M = O/I \qquad \text{......(1).}$$

Under the prevailing conditions of brightness (which are not altered by a perfect instrument) the eye with the effective pupil ω has a limit of separation s which is given by the above experiments. Transformed to the object space this limit be-
S comes S, and it is this quantity which concerns us in judging the properties of the system formed by the instrument and the eye together. We have

$$S = s/M \qquad \text{......(2).}$$

We must distinguish the case in which the exit pupil is smaller than the pupil of the eye from that in which it is larger; the value of ω which must be taken for calculating s is different in the two cases.

Case 1. Exit pupil of the instrument smaller than the pupil of the eye, $I < \omega_0$. This is the more common case. Then the pupil actually used is that of the instrument ($\omega = I$) and the whole of the objective is utilized ($\Omega = O$). Equations (1) and (2) then give

$$s\omega = S\Omega \qquad \text{......(3).}$$

The left-hand side is the specific limit of the eye under the given conditions; the right-hand side $S\Omega$ or SO may be called the specific limit of separation of the
σ, Σ combination, instrument and eye; these quantities being called σ and Σ, we have

$$\sigma = \Sigma.$$

The perfect instrument is that which does not spoil the specific properties of the eye.

Case 2. $I > \omega_0$.

Here the pupil of the eye is fully utilized and $\omega = \omega_0$. The preceding relations give

$$\Sigma = \sigma I / \omega_0.$$

If the magnification is changed, then I is altered without any variation of the pupil ω_0 or σ; as long as the relation $I > \omega_0$ remains true, the curve giving Σ as a function of I is a straight line passing through the origin.

Similar considerations apply to the microscope, but here we practically always have the first case.

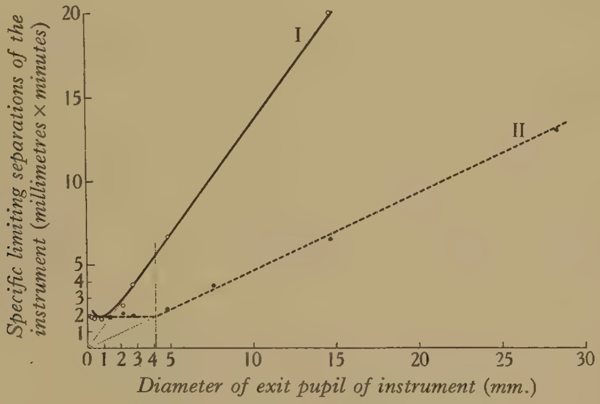

Figure 10. Curves showing the specific limiting separation for perfect instruments, as a function of the exit pupil. Normal eye, full curve; perfect eye, dotted curve. The diameter of the pupil of the eye is constant and equal to 4·05 mm.

Experimental verification. The preceding results have been verified by Mr Arnulf by means of a small telescope with a very good objective of diameter $O = 30$ mm. and a focal length $f = 285$ mm., by Hilger; a number of eyepieces giving magnifications from 1 to more than 1000 were used; for the lowest magnifications the eyepiece was another lens similar to the objective; then oculars of the usual types, and finally, for the highest powers, a microscope objective was used as eyepiece. In order to avoid possible variations in the diameter of the pupil of the eye, a circular diaphragm 4 mm. in diameter was always used. As test object, parallel lines with complete contrast ($\gamma = 1$) and high brightness were used. In each case the limit of separation was determined, and from it the specific limit Σ of the combination of the eye and instrument was deduced. The results are represented in a diagram in which the abscissae are the diameters of the exit pupil of the telescope (a quantity which varies as $1/M$, where M is the magnification) and the ordinates are the specific limits of separation. The theoretical curve consists of two parts: a linear part passing through the origin for all values of I greater than 4 mm., and a curved part for cases in which $I < 4$ mm. In the latter part we should have $\Sigma = \sigma$, and the curve is the same as that deduced from naked-eye observations (figure 3). In figure 10, the full-line curve is the theoretical one; the observed values are shown by small circles. The agreement is very satisfactory.

If the eye were an instrument perfect in all respects and limited solely by diffraction we should still find two parts, but different from those given by the real eye. Curve II of the same figure (in dotted lines) represents the theoretical curve for this case; the part corresponding to $I < 4$ mm. gives a constant ordinate. To verify this conclusion, Mr Arnulf has constructed a model of a perfect eye as follows. At the end of the telescope studied, with its 4-mm. pupil in position, he placed a good objective of focal length 1 m. which, stopped down by the artificial pupil of diameter 4 mm., may be considered as perfect. The real image from this objective is projected on a ground glass, which acts as the retina. The effect of grain is eliminated by moving the glass rapidly. The image is examined by means of a magnifying-glass. Owing to the size of the final image on the retina all the imperfections of the eye disappear. In figure 10 the black points give the observed values; they are in excellent agreement with the theoretical curve.

§ 9. OPTIMUM CONDITIONS FOR OBTAINING A GIVEN EFFECT

It is desired to construct a telescope having a given limit of separation S for a given brightness and contrast. Two fundamental quantities must be chosen, the diameter O of the objective and the magnification M. Naturally, the smallest possible diameter of objective will be selected.

We will consider the case where the exit pupil is smaller than the pupil of the eye ($I < \omega_0$). Then $S \times O = \sigma$; the quantity σ refers to the naked eye for the pupil ω equal to I and the given brightness and contrast. This quantity σ is known from the above-mentioned curves as a function of I. Usually the curve giving σ as a function of ω has a minimum; this minimum corresponds to the most advantageous design. It determines the value of the exit pupil of the instrument as well as that of σ. The diameter of the objective is determined by equation (3), which gives $O = \sigma/S$, and, the exit pupil being known, we have the magnification $M = O/\omega$.

For high and medium brightness (e.g. between 1·5 and 0·10 stilb) the minimum of the specific limit of separation σ occurs for effective values of the exit pupil lying between 0·5 and 0·8 mm., whatever the contrast; we may reasonably take 0·7 mm. This leads to a magnification of 100 for an objective of diameter 70 mm. This is in accordance with the practice of astronomy for the observation of really bright surfaces like the moon and the major planets. Similar considerations apply to the microscope, for which exit pupils of the same order as those in practice are found. In the telescope, the objective diameter can be calculated from the limit of separation for a given contrast.

For the lower brightnesses, from 10^{-3} to 10^{-5}, the minimum of σ moves progressively towards large pupils, and the more so the smaller the value of B. For a fairly good contrast, say for $\gamma = 0{\cdot}3$, the optimum occurs for an exit pupil between 1 and 2 mm., which may rise to 4 mm. for the faintest contrasts.

Finally, for the lowest brightness, less than 10^{-8}, there is an advantage in taking the exit pupil as large as the pupil of the eye.

§10. TELESCOPES FOR TERRESTRIAL OBSERVATION AT NIGHT

The most characteristic case of observation at low brightness is that where objects are seen on a moonless night, with no other illumination than that from the sky. The brightness of the sky is of the order of 10^{-8} stilb, and that of objects on the ground is still less. It is well known that under these conditions visibility is very bad; only objects of great apparent diameter are seen. Let us consider for example a brightness of $0{\cdot}4 \times 10^{-8}$ and a test object of perfect contrast. Binoculars of the usual type may have for example a magnification of 8, with an objective of 32 mm. The preceding formulae lead to 14′ as the limit of separation; vision is much worse than naked-eye vision in daylight.

If we could use much larger instruments without being stopped by consideration of weight, inconvenience and price, we could considerably improve vision at night. Take the same test object and consider how a telescope should be constructed to give at this feeble brightness the same limit of separation as the naked eye in full daylight, i.e. a limit of 1′. We find that this result is attained with a 26-cm. objective and a magnification of 86. This is a large instrument whose employment would generally be impossible. And again, the brightness adopted is not the least which might be encountered. For $B = 1{\cdot}3 \times 10^{-10}$, it is found that the same result would be reached with a 250-cm. (100-in.) objective and a magnification of 250.

For strong brightnesses (daylight vision) the necessity for large pupils and large instruments is again found when the contrast is only slight. Take for example $B = 0{\cdot}15$ stilb (which is a very good brightness for objects in sunlight) but a very feeble contrast, $\gamma = 0{\cdot}02$. We wish to attain a limit of separation of 5″. This is found to require a 92-mm. objective and a magnification of 21.

§11. IMPERFECT INSTRUMENTS

Let us take certain defined conditions of brightness and contrast and consider the specific limits of separation. A perfect instrument would give a limit Σ equal to the limit σ for the naked eye under the same conditions and for the same pupil-aperture; we have therefore $\Sigma = \sigma$. Now examine an imperfect instrument, and we find that it has a larger limit Σ' and we set $\Sigma' = \sigma'$ for the eye. The ratio $E = \sigma/\sigma'$ is called by Mr Arnulf the efficiency of the instrument; this definition allows the properties of entirely different instruments, such as a microscope and a telescope, to be compared with each other; nevertheless, it must be remarked that this efficiency depends greatly on the brightness and the contrast of the test object employed. Experiment shows that for test objects with complete contrast ($\gamma = 1$) and great brightness, as those of Foucault usually are, the efficiency nearly always has a value near 1, i.e. nearly all instruments appear to be almost perfect. This is not so if the brightness and contrast are lowered; measurement of the efficiency then permits the classification of instruments.

The imperfections of an instrument, which are marked by a decrease in E, can arise from two causes—(1) aberrations of all kinds, and (2) the presence of stray light. The latter effect is shown particularly at low values of the contrast. Suppose that a test object which has a background of uniform brightness B on which lines with a contrast γ are superposed is being examined. Stray light has the effect of K adding a brightness KB over the whole field, where K is a stray-light coefficient. This has the effect of lessening the contrast of the marks, giving it the value

$$\gamma' = \gamma/(1+K).$$

This decrease in contrast has the effect of increasing the limit of separation, and the change is large if the contrast γ is already slight. The following table refers to a brightness B equal to 0·01 and a pupil ω equal to 0·54 mm.; it gives the values s of the limit of separation for different values of the contrast of the test object, for the values $K=0$ (absence of fogging) and $K=1$ (brightness of the stray light equal to that of the background).

Table

γ	s	
	$K=0$	$K=1$
1	3·9′	4·4′
0·1	6·1′	10′
0·05	10′	∞

The influence of stray light is slight when $\gamma=1$; it becomes rather large when $\gamma=0·1$, and when $\gamma=0·05$ fogging causes the complete disappearance of the test object.

This partly explains the difference between a laboratory test of an instrument and the use of the same instrument in the open air. In the former case a test object with great contrast is generally used on a dark background, which almost completely removes the effect of stray light; in the open air there are many objects with slight contrast, and stray light is of importance.

§ 12. RESULTS OF AN EXPERIMENTAL STUDY OF EFFICIENCY

The Adam Hilger objective previously mentioned was first studied. The diameter was 31 mm., the focal length 285 mm. and the aperture $f/9$. The objective was examined with various values of γ, with a well illuminated test object. Curve I of figure 11 gives the value of the efficiency. It will be seen that the efficiency is nearly always equal to 1, except at very slight contrasts where a slight fall is shown. The same objective, reversed, was then tested, so that a longitudinal spherical aberration of 3 mm. was introduced. Curve III gives the results obtained. Curve II refers to a simple non-achromatic lens, under the conditions in which it gave the best definition. It will be seen that when $\gamma=1$ the efficiency of the very bad instruments is sensibly equal to that of the perfect objective. But as the contrast diminishes, the differences in properties are brought out strongly.

Curve IV concerns the same simple lens, but with observations at the *circle of least confusion.* Under these conditions the images are very poor, and the low efficiency is shown even for a contrast of unity.

It may be concluded that laboratory examination of optical instruments could give information useful in practice if test objects with variable contrast were used.

It would also be of importance to examine the effect of stray light systematically. This light can occur in several ways. It can emanate from the actual object under examination, by scattering at the surfaces and in the material of the optical parts. It may also originate from light travelling in all directions, scattered in the instrument. Figure 12 shows the outline of an arrangement used by Mr Arnulf for the study of stray light. The test object, a transparency on glass, is illuminated by the opal glass lamp *L*, with the interposition if desired of a filter *E* to reduce the brightness. The test object is surrounded by the diffuser *F*, illuminated by lamps (not shown), and limited by an adjustable diaphragm *I*. We have thus the equivalent of an object of greater or less brightness, surrounded by a background whose brightness and area can also be varied. Finally, the diffusing sphere *S*, illuminated by lamps (not shown), gives the equivalent of the general light which is found in the open air.

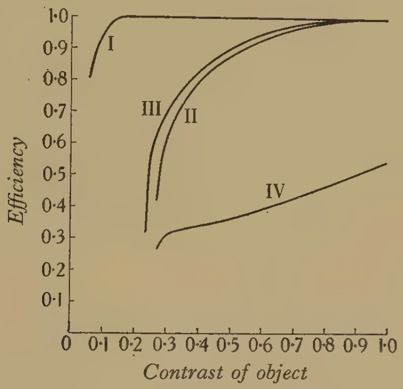

Figure 11. Variation of efficiency with contrast. I, excellent Hilger objective, $f=285$ mm., $O=31{\cdot}2$ mm.; II, simple plano-convex lens of same properties, at minimum of aberration; III, objective 1 reversed, spherical aberration approximately 3 mm., set at marginal extremity of axial sheet of caustic; IV, as III, set at the common point of the two sheets of the caustic.

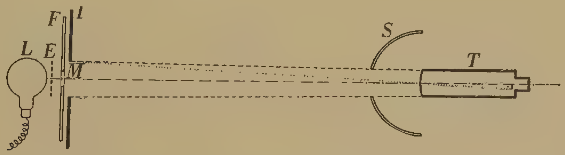

Figure 12. *L*, opal lamp illuminating test object; *E*, absorbing screen controlling brightness of test object; *M*, transparent test object; *F*, diffusing disk surrounding test object (lighted by lamps not shown); *I*, variable circular diaphragm, leaving exposed a diameter of the disk *F* corresponding to the field of the telescope *T*; *S*, diffusing sphere, whose illumination is not represented, supplying general light to illuminate instrument outside its field.

§ 13. CONCLUSION

The preceding considerations will, I hope, have shown the importance of the properties of the eye in deciding what it is possible to *see* in an optical instrument. The practical constructor of optical instruments is forced to take many other factors into account, in particular weight, convenience of handling, conditions of use, and price; further, it is impossible for him to build a different instrument for each particular case. Certain cases, such as that of night observation, may derive benefit from the considerations set out above. On the other hand, users of instruments may make use of them by not asking of an instrument services which it cannot render.

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THE PHENOMENON OF SPREADING IN THE FIRST POSITIVE BANDS OF NITROGEN

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ABSTRACT. The paper describes an experiment designed to distinguish between two theories of secondary excitation of the first positive bands in nitrogen. The resonance radiation of nitrogen emitted from an electron beam is allowed to pass through a thin celluloid window which holds back metastable atoms. The results show that part, and possibly the whole, of the secondary excitation of the first positive bands is due to collisions of the second kind with molecules in the $a^1\Pi$ state.

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§ 1. INTRODUCTION

It is well known that if an electron beam is projected into a gas at low pressure the light emitted is in general not confined to the beam. Some of the spectral lines are emitted at distances so far from its edges that they cannot possibly have been excited by direct electron-impact. Another group of lines, on the other hand, is emitted only from gas molecules actually within the beam, and for these we may assume that excitation is direct. The first group of lines we may call the *spreading lines*, the second the *non-spreading lines*. Spreading has been observed in mercury(1), in helium(2) and in nitrogen(3). This paper describes an investigation of the mechanism of spreading for the first positive bands of nitrogen.

The secondary excitation process responsible for the production of spreading has been explained in two different ways by Maxwell(1) and by Skinner and Lees(2) respectively, and it is perhaps worth while to give here a brief summary of the essential points in the two theories.

Both theories agree that the spreading of resonance lines and of lines whose upper level is an upper level of a resonance line is due to absorption in the gas of resonance radiation produced by direct excitation in the electron beam. In helium, for example, this absorption produces atoms excited to ^1P states in the gas outside the beam, and these atoms can reradiate either the original resonance line or any line whose upper level is ^1P. This explanation agrees with the experimental observations. All lines starting from ^1P levels show strong spreading.

But there exist also lines which show strong spreading and whose upper levels cannot possibly be excited by optical absorption. Maxwell explains this by assuming that metastable atoms produced in the electron beam (either by direct excitation or by cascade) diffuse outwards into the body of the gas. They can here absorb radiation from the beam, be raised in this way to a still higher level and so radiat the other spreading lines.

The grave difficulties in the way of Maxwell's explanation have been exhaustively discussed in the case of helium by Skinner and Lees(2) who propose a alternative explanation for the occurrence of the anomalous lines. They sugges that in these cases the spread light arises from collisions of the second kind betwee atoms in the ground state and atoms which have been raised to resonance level outside the electron beam. Through these collisions atoms can be transferred t energy levels they could not reach by optical absorption; and so lines can sprea which are not resonance lines. The Skinner-Lees theory is entirely consistent wit the numerous experimental facts; but there was no absolute proof that it wa correct.

The only way to distinguish certainly between the two theories was to arrang some experiment in which the whole light from the beam was allowed to pass int the surrounding gas and at the same time the diffusion of metastable ions wa prevented. In the experiments to be described, the resonance radiation of nitroge was allowed to pass through windows of extremely thin celluloid which partiall transmitted radiation of all wave-lengths, at the same time holding back metastabl atoms. Maurer and Wolf(4) have previously used a somewhat different method o eliminating metastable atoms and have rendered it practically certain that th explanation of Skinner and Lees is correct in the case of helium. Nevertheless i seemed worth while to carry out the investigation by a different method in th case of nitrogen, which shows certain peculiarities and for which a different mechanism might be at work. The resonance radiation of nitrogen extends from 145 to below 1200 A. Fluorite completely absorbs the short-wave-length end of this spectrum, and where it transmits has a rapidly varying absorption coefficient Celluloid had to be employed to make sure of getting the whole wave-length range.

§ 2. APPARATUS

Attempts to use low-pressure arcs in nitrogen as sources of resonance radiation were unsuccessful. For technical reasons it proved impossible to bring the main body of the discharge within a distance less than 4 cm. from the aperture of the resonance chamber without at the same time introducing electrons from the discharge. As the arcs would not run steadily at a pressure of less than 5×10^{-3} mm. of mercury the long column of gas must have absorbed strongly. No effects were observed, and the method was abandoned.

The experimental tube. We therefore returned to the original tube described in the paper of Thompson and Williams(3). The experimental arrangements were essentially as described there except that the Faraday collector took various forms as the work progressed. The tube is shown diagrammatically in figure 1. The electrons are accelerated from the equipotential cathode K to the first slit S by a voltage V_1, about 115 volts. They then pass in succession through the focusing slit F whose potential V_2 can be varied to give the sharpest beam and through the defining slit C whose voltage V_3 gives the final energy of the electrons in the beam. The Faraday box X collects the electrons and the milliammeter MA measures the current in the beam.

The Faraday cage first used was of the form shown in figure 1. The beam, the axis of which is shown dotted, thus passed parallel to the upper surface of X within a distance of 1 or 2 mm. With this arrangement it was found possible to produce a distinct tuft of spread light above the small aperture A cut in this surface. The pressures of nitrogen in the tube varied between 3 and 4×10^{-3} mm., and the beam currents between 2 and 3 mA.

Some preliminary attempts to observe spreading through a thin celluloid film, with a collecting-electrode essentially similar to that shown in the figure, were unsuccessful owing to the films breaking under the action of the discharge.

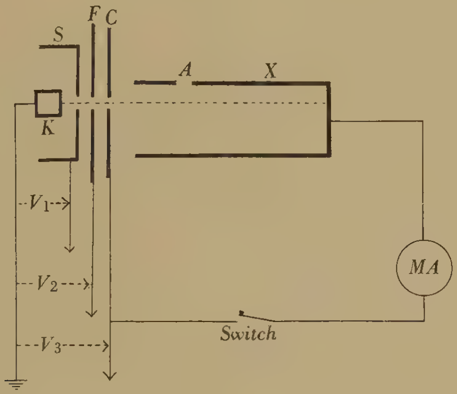

Figure 1.

The windows, which were of the order of 10^{-6} cm. thick, were prepared as described by O'Bryan(5). A dilute solution of celluloid in amyl acetate was allowed to spread over a clean surface of distilled water, and after the solvent had evaporated a metal frame which was to carry the window was dropped on the film which adhered to it. The frame was then picked off and allowed to dry.

The windows so prepared usually appeared perfectly transparent. They were just visible by reflected light when held over a black background, and often presented a flawless surface when so examined. But some of them showed very faint silvery streaks covering perhaps a tenth of the total surface. These were perhaps due to traces of grease on the surface of the water; in any case they tended to disappear as the technique of cleanliness improved. It is worth pointing out, nevertheless, that some of the early, apparently imperfect windows turned out to be far more durable than the cleaner windows afterwards produced.

Although this form of collector proved ultimately unsuitable, the experience gained with it, and with other preliminary types, was useful in finding the best conditions under which spreading occurred. Moreover these early investigations showed that the rupture of the celluloid was not due to mechanical shock when the apparatus was pumped out, that the windows could be stored *in vacuo* for periods o days, and that heating by radiation from the rather large hot cathode did not injure them. On the other hand a quite small current (10^{-4} A.) in the electron beam destroyed them in a few minutes, even though they were protected from the direc beam by a barrier. Thus there remained the possibility either that the windows had been charged up by the capture of electrons and were torn by electrostatic forces at their edges, or (what is more probable) that the slow electrons produced some chemical disintegration when they struck the film.

It was therefore necessary to design a collecting-box and resonance chamber in which the windows could be protected during the preliminary manipulation of the electron beam, and only exposed while an observation was actually being made.

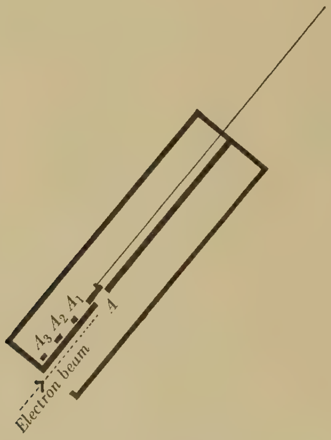

Figure 2.

Final form of the apparatus. The final form which the electrode took is shown diagrammatically in figure 2. A stainless-steel box was divided longitudinally by a metal septum. In this septum was a single circular aperture A, $2\frac{1}{2}$ mm. in diameter. The sides of the box were closed with thin glass windows carefully cleaned. Thus it was impossible for metastable atoms to diffuse into the resonance chamber without first striking a metal surface unless they passed through the aperture in the septum. This aperture could be closed by a rectangular metal slide moving in a longitudinal depression cut in the septum. The axis of the tube was tilted at an angle of 45° to the horizontal, so that the slide rested in equilibrium at the lowest point of the resonance chamber and closely in contact with the septum. This slide carried the celluloid windows. When it was in the extreme position as shown in the figure it closed the aperture. By means of a thin copper wire it could be drawn up so as to register the three holes A_1, A_2, A_3 in succession with the aperture in the septum. This operation could be performed when the electrode was inside the tube by means of a windlass and a greased joint. A circular scale on the windlass made it possible to say which window was in registration with A. Thus the preliminary adjustments of the electron beam could be made while the celluloid windows on the slide were effectively screened from any direct action of the discharge. A switch was provided in the circuit from this electrode assemblage, figure 1, so that the electron beam could be quickly interrupted when necessary.

The apertures A_2 and A_3 were covered with a fine wire gauze made from No. 47 Eureka wire spot-welded into place. This had two purposes. First, it made the very thin windows afterwards used very much stronger mechanically. Secondly, it was hoped that the gauze would assist in conducting away any electrostatic charge which might be built up on the celluloid. The gauze had a mesh of $\frac{1}{2}$ mm. It was made by sandwiching a grid of Eureka wire between two copper flats and passing a gradually increasing current from a welding transformer through the assemblage. Alcohol was used as a flux. In this way the crossed wires were welded together at their intersections, and the gauze remained smooth.

The greatest care was taken to avoid contaminating either the slide or the Faraday collector with grease. On this account, the Faraday collector was never touched with the fingers except during a periodical readjustment of the whole electrode system. The slide was heated to about 300° C. in air before being covered with the celluloid windows, and after this treatment it was allowed to come into contact only with clean filter paper and previously heated forceps. Unless these precautions were rigorously observed, traces of grease would subsequently make their way on to the inner surface of the collecting-electrode and there become charged up by collecting scattered electrons from the beam. Local retarding-potentials were thus produced which rendered the electron beam diffuse and inhomogeneous in velocity. The grease could only be removed by long bombardment with heavy electron current.

The apertures were covered by celluloid windows in the manner already described, the slide was hooked to the copper wire and manipulated into its groove. The electrode assemblage, which was carried on a ground joint, was then returned to the tube.

§ 3. OBSERVATIONS

The routine of observation was as follows. The tube was pumped down after the windows had been inserted, and the cathode was outgassed with no accelerating potentials on any of the slits. Nitrogen was now streamed through at a pressure of about 4×10^{-3} mm. and the intermediate slits were cleaned up by passing a heavy current (up to 200 mA.) to them from the filament. During the process the switch in the collector circuit was left open so that no electron beam passed through the Faraday collector. Even with the switch open there remained a faint luminosity due to a beam of positive ions as described by Thompson and Williams(3). In the earlier stages of the discharge it had a greenish colour and presumably consisted of positive ions of mercury, an impurity which could otherwise be easily detected by using an electron beam too slow to excite the spectrum of nitrogen, and examining the light with a small spectroscope. The prominence of the mercury spectrum in the ion beam is presumably to be explained by a much higher efficiency of ionization for mercury than for nitrogen under the given discharge conditions. In any case this light became much fainter after the tube had run for half an hour, and negligible compared with the nitrogen light emitted by the direct electron beam. An appreciable amount of mercury vapour seemed to inhibit the spreading of the first positive bands, even though the mercury spectrum appeared very much fainter in total intensity than the nitrogen spectrum, and it was found worth while in consequence to admit air into the tube when necessary in such a way that mercury vapour could not be carried over from the liquid-air trap.

The beam was now allowed to pass into the Faraday box by closing the switch, and it was made as sharp as possible by altering the position of the cathode or the potential of the focusing-slit. The energy of the electrons in the beam was usually between 17 and 19 volts, and the current from 3 to 4 mA. The voltage was usually adjusted to give the best compromise between a good beam and intense spreading. In all the final experiments a low-voltage beam was employed in the manner described above. Some of the earlier experiments were carried out with a high-voltage beam, because larger currents can be readily obtained at, say, 50 volts than at 18 volts, yet the intensity per milliampere of the spread light is fainter. A more serious objection to the high-voltage beams was their great tendency to instability at high current-densities and high pressures. It seemed to be due to a form of very high-frequency oscillation such as has already been described in connexion with low-voltage arcs. In its limiting form it showed up as a sudden increase in the brightness of the beam, which, however, retained the characteristic purple colour of the negative bands (N_2^+) and of the second positive bands. Around it was a strong pinkish glow quite different in appearance from the ruddy spreading of the low-voltage beam, and containing not only the first positive but also the second positive bands. On the opening of the switch so that no resultant current could flow to the Faraday cage, the beam would frequently only alter slightly in appearance, although no current could flow through the milliammeter. There were, however, less pronounced forms of the same behaviour, characterized by abrupt alterations in the character of the beam as the accelerating potential was slowly altered. With the 18-volt beam, however, none of these phenomena were observed; there was a steady alteration in the brightness and shape of the beam as the voltage was altered, and (provided the collector box was free of grease) the excited light disappeared throughout a range of less than a quarter of a volt when the potential fell to the critical voltage.

As soon as conditions were satisfactory, all direct light from the filament and from the discharge was screened from the observer's eye; the beam was switched off, and the aperture A_1 was brought into registration with the hole in the septum. This aperture carried no gauze, and usually the celluloid film on it was deliberately demolished before it was put into the tube, although in fact it seldom resisted exposure to the side of the beam for more than half a second. The beam was then switched on, and the spreading into the resonance chamber was examined. It showed as a faint tuft of ruddy light escaping into the resonance chamber throug the open aperture. If the spreading seemed strong enough the beam was switche off, and the celluloid window A_2 was brought into registration with the hole. The beam was then switched rapidly on and off, the resonance chamber being meanwhile examined for spreading. The same observation was then made through A_3 and the results were noted down. The nitrogen stream was then stopped, air was let into the apparatus, and the condition of the windows on the slide was examined. Usually several panes of the celluloid were ruptured even with this brief exposure to the beam, but in one or two lucky cases the window remained more or less intact. Visual observation had to be employed because of the extremely short life of the windows under the given discharge conditions.

§ 4. RESULTS

The early series of experiments using windows 10^{-6} cm. in thickness showed no apparent spreading into the resonance chamber through the celluloid, even though one or two panes (about $\frac{1}{10}$ or more of the surface) were broken when the slide was examined afterwards. Rough estimates suggested that if the light in the resonance box had been as small as $\frac{1}{6}$ of the original intensity it would have been detectable. O'Bryan's absorption curves give a transmission of at least $\frac{1}{3}$ for the Lyman resonance radiation for windows 10^{-6} cm. thick. Since on the Skinner-Lees theory of spreading the intensity of the spreading should be proportional to that of the resonance radiation, these results seemed to be rather opposed to that theory. However, on one occasion a somewhat more dilute solution of celluloid, giving windows $0{\cdot}8 \times 10^{-6}$ cm. thick, was prepared. With a rather strong beam (5 mA.) a faint spreading into the resonance chamber through the window could be seen. Although the window was not quite intact on removal this provisional positive result gave encouragement for further investigation.

In all subsequent experiments windows only 5×10^{-7} cm. in thickness were used. Celluloid films of this tenuity are very fragile. They have also proved somewhat less resistant to the destructive action of the discharge than have the thicker windows. A large number of trials of the thin celluloid windows were made after experimental conditions had been made as good as possible. In only two experiments were windows removed intact, and in these cases faint spreading into the resonance chamber was definitely noticed. But the positive evidence for spreading through the celluloid does not rest only on these two observations. Several more observations of spreading, about 8 in all, were made through windows punctured only at one point, and with about 90 per cent of their surface unbroken. In these cases also spreading could be seen extending over the unbroken surface of the window. There is therefore good evidence to the effect that this form of spreading does take place through thin celluloid windows.

§ 5. DISCUSSION OF RESULTS

For the purposes of reference a diagram of the relevant energy levels of nitroge is given, figure 3⁽⁶⁾. The band system with which we are concerned arises fro the transition $B^3\Pi \rightarrow A^3\Sigma$, and most of the bands which contribute intensity to th visible radiation originate on levels below the twelfth vibrational level of the ^{3} state. The second positive bands, which do not show spreading, correspond to th transition $C^3\Pi \rightarrow B^3\Pi$. The only strong singlet system which can concern us is th Lyman-Birge-Hopfield system $a^1\Pi \rightarrow X^1\Sigma$; bands of this system whose lower leve is the ground level of nitrogen form the resonance bands. The Vegard-Kapla system $A^3\Sigma \rightarrow X^1\Sigma$ is the only known intercombination*; it is extremely weak an is excited only under special conditions. Thus the $A^3\Sigma$ level is for practical purpose metastable.

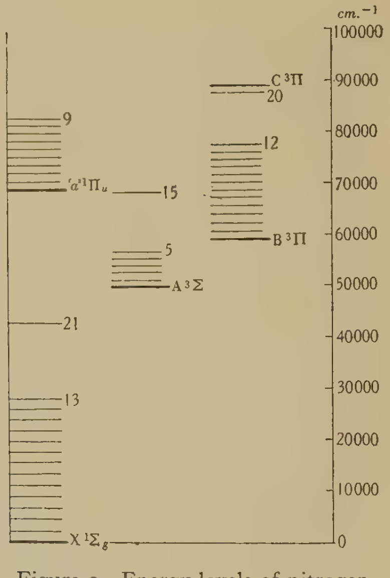

Figure 3. Energy levels of nitrogen.

Thus spreading could be explained *a priori* as due either to collisions of th second kind or to absorption by metastable molecules. Our experiment show however, that at least some part of the secondary light is due to the former process There arises here the apparent difficulty that if such collisions are to occur befor the molecule in the $^1\Pi$ state reradiates normally, then the effective cross section o the molecule in this state for a collision of this type must be some hundreds o times as great as the gas-kinetic cross section of the normal molecule. But thes very large effective cross sections are not uncommon. It is known that if, during collision of the second kind, most of the energy of excitation of the one molecule i transferred as excitation energy to the second molecule, so that little of the original energy goes into kinetic energy of translation, then the process may become extremely probable. This was predicted theoretically by Kallman and London(7) and verified experimentally by Duffendack(8) for atomic collisions. The latter reports effective cross sections which may be as much as 10^5 times larger than the gas-kinetic area. It is clear from figure 3 that a molecule in any of the vibrational levels of the $^1\Pi$ state can transfer its energy to excite lower states of the $B^3\Pi$ level. Moreover, owing to the very closely spaced vibrational-rotational levels of the ground state, the excess energy can remain as energy of vibration and rotation; and the condition for a large effective cross section is satisfied.

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* This intercombination fixes the A level with respect to the ground state X.

There remains the question whether the whole of the secondary light is to be explained by the mechanism suggested. It is of course impossible to make any definite statement on this point without a photometric comparison of the intensity of the secondary light with and without the interposition of the celluloid window. Although it has been pointed out in the discussion of the results that the intensity seemed to be reduced by the celluloid somewhat more than was to be expected on the basis of O'Bryan's absorption coefficients, nevertheless too much weight cannot be attached to this fact in view both of the difficulty of comparing visually the intensity of two light-sources near the threshold of visibility, and of the fact that the transmissibility of the films seemed to vary somewhat with their mode of preparation.

§ 6. ACKNOWLEDGMENT

I take the opportunity here of expressing my sincere thanks to Mr S. E. Williams who collaborated with me for a time during the earlier part of this work.

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AN IMPROVED NUMERICAL METHOD OF TWO-DIMENSIONAL FOURIER SYNTHESIS FOR CRYSTALS

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ABSTRACT. It is shown that a two-dimensional Fourier summation for a crystal without a centre of symmetry can be resolved into one-dimensional summations, and these latter can be calculated very rapidly by using a set of printed strips which give cosine and sine waves of different wave-lengths and amplitudes. The most useful interval of division of the strips, and various features concerning their use, are described.

§ 1. INTRODUCTION

A METHOD has been described by J. M. Robertson$^{(1)}$ whereby the summation of a two-dimensional Fourier series is reduced to the processes of first arranging sets of figures, and of then adding them. The method described in the present paper is similar to this, but the process of arrangement is very greatly reduced, and since most of the time taken is concerned with the additions it is claimed that the method is as quick as any numerical method can possibly be.

The method is based on that described by the authors$^{(2)}$. Essentially this reduces the computations to the addition of a number of one-dimensional cosine and sine terms. There are thus only two variables, the amplitude and wave-length of each cosine or sine wave, and the number of combinations of these to cover most cases is sufficiently small for it to be practicable to prepare them in advance. This has been done by the authors, the numbers representing the various waves being printed on cardboard strips. The present paper describes the derivation and use of such a set of strips.

§ 2. THEORETICAL CONSIDERATIONS

Division of the area of the projection. It has been shown$^{(3)}$ that if a radiation of λ, θ wave-length λ be used, and if all reflections with glancing angles less than θ be observed, then Fourier synthesis will not show any detail finer than $0{\cdot}6\lambda/2 \sin \theta$. If $\lambda = 1{\cdot}54$ A. (for $K\alpha$ radiation of copper) and $\sin \theta = 1$, this quantity is $0{\cdot}46$ A. Thus it is necessary that the points at which the electron-density is computed should be appreciably closer together than this; but any undue closeness will be unnecessary as it will not reveal any greater detail.

Thus for most ordinary projections, the edges† of which are between 8 and 15 A., division into about 50(4) parts would be suitable. This number, however, has some isadvantages. For instance points with co-ordinates $\frac{1}{4}$ are not included explicitly, nd it is sometimes important that the electron-density at such points should be nown accurately. This defect may be overcome by dividing the edge into 48(5) or 0(1) parts, and this also makes the work of preparation of the tables rather lighter. he latter number was chosen because it extends the limit of applicability of the ethod somewhat.

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† These will not be the edges of the unit cell unless the crystallographic axes are orthogonal.

Adaptability to extreme cases. The division of the cell-edges into 60 parts is irectly suitable if the maximum indices are each between 11 and 20. If one of the aximum index-values is below 11 (i.e. if one cell-dimension is small) it will be dvisable to make the interval of division of the corresponding edge $\frac{1}{30}$. This may e done most simply by considering that we are going to perform a synthesis of two nit cells, the short edge being considered as doubled. One of the indices of each lane referred to this doubled cell will be doubled. Thus all we have to do in order to btain an interval of $\frac{1}{30}$ in any direction is to double the corresponding indices of the 's and proceed in the usual way. The strips will then give the projection over the ange 0 to 0·50 directly, instead of from 0 to 0·25. Similarly, if the maximum index n one direction is 6, the indices corresponding to this direction may be trebled, and he interval of division will be $\frac{1}{20}$. The general rule is that the tables should be used s near as possible to their maximum index 20.

If, on the other hand, the maximum index exceeds 20 the strips as prepared by he authors will not be comprehensive. It will be desirable to make the interval of ivision $\frac{1}{120}$, in which case the indices must be halved. Thus the odd indices cannot e included, and their contribution will have to be computed by the ordinary ethod. Nevertheless, unless both ranges of index are greater than 20, it will be ossible to use the strips directly in the final tables which involve the greater part of he work.

Expression of the general case in terms of one-dimensional series. The most general ase (so long as the wave-length used is not near an absorption edge of any of the toms concerned) is that of the completely asymmetric projection, in which the only elation between the Fs is $F(hk0) = F^*(\bar{h}\bar{k}0)$, where F^* is the conjugate complex of F. The direction of projection is taken as parallel to the c axis.

F, F^*, h,

If x and y are the co-ordinates of any point in the projection in fractions of 2π, nd H and K are the maximum values of h and k in the array of Fs, the summation equired is as follows, $F(hk)$ being now written for $F(hk0)$

x, y

H, K

$$\sum_{-H}^{H}\sum_{-K}^{K} F(hk) \exp i(hx+ky)$$

$$= \sum_{-H}^{H}\sum_{1}^{K}\{F(hk)\exp i(hx+ky) + F^*(hk)\exp -i(hx+ky)\}$$

$$+\sum_{1}^{H}\{F(h0)\exp ihx + F^*(h0)\exp -ihx\}$$

$$+F(00).$$

Since $F(hk)$ and $F(\bar{h}\bar{k})$ are conjugate, they may be expressed respectively a
δ $|F(hk)|\exp i\delta(hk)$ and $|F(hk)|\exp -i\delta(hk)$, and the expression becomes,

$$\sum_{-H}^{H}\sum_{1}^{K}|F(hk)|\{\exp i[hx+ky+\delta(hk)]+\exp -i[hx+ky+\delta(hk)]\}$$

$$\sum_{1}^{H}|F(ho)|\{\exp i[hx+\delta(ho)]+\exp -i[hx+\delta(ho)]\}$$

$$+F(oo)$$

$$=2\sum_{-H}^{H}\sum_{1}^{K}|F(hk)|\cos[hx+ky+\delta(hk)]+2\sum_{1}^{H}|F(ho)|\cos[hx+\delta(ho)]$$

$$+F(oo).$$

C Let $$|F(hk)|\cos\delta(hk)=C(hk)$$

S and $$|F(hk)|\sin\delta(hk)=S(hk).$$

Then we have

$$\begin{aligned}&2\sum_{-H}^{H}\sum_{1}^{K}\{C(hk)[\cos hx\cos ky-\sin hx\sin ky]\\&\qquad-S(hk)[\sin hx\cos ky+\cos hx\sin ky]\}\\&+2\sum_{1}^{H}\{C(ho)\cos hx-S(ho)\sin hx\}\\&\qquad+F(oo)\end{aligned}$$

which, for the purposes of summation is put into the form

$$\begin{aligned}&2\sum_{1}^{H}\sum_{1}^{K}\{C(hk)[\cos hx\cos ky-\sin hx\sin ky]\\&\qquad-S(hk)[\sin hx\cos ky+\cos hx\sin ky]\\&\qquad+C(\bar{h}k)[\cos hx\cos ky+\sin hx\sin ky]\\&\qquad(\bar{h}-Sk)[-\sin hx\cos ky+\cos hx\sin ky]\}\\&\quad+2\sum_{1}^{K}\{C(ok)\cos ky-S(ok)\sin ky\}\\&\quad+2\sum_{1}^{H}\{C(ho)\cos hx-S(ho)\sin hx\}\\&\qquad+F(oo)\\&=2\sum_{1}^{H}\sum_{1}^{K}\{[C(hk)+C(\bar{h}k)]\cos hx\cos ky\\&\qquad-[C(hk)-C(\bar{h}k)]\sin hx\sin ky\\&\qquad-[S(hk)-S(\bar{h}k)]\sin hx\cos ky\\&\qquad-[S(hk)+S(\bar{h}k)]\cos hx\sin ky\}\\&\quad+2\sum_{1}^{K}\{C(ok)\cos ky-S(ok)\sin ky\}\\&\quad+2\sum_{1}^{H}\{C(ho)\cos hx-S(ho)\sin hx\}\\&\qquad+F(oo).\end{aligned}$$

The preliminary tables would then be concerned with the evaluation of

$$2\sum_{1}^{H}\{C(h0)\cos hx - S(h0)\sin hx\} + F(00) = A(0, x), \text{ say,} \tag{A}$$

of

$$2\sum_{1}^{H}\{[C(hk)+C(\bar{h}k)]\cos hx - [S(hk)-S(\bar{h}k)]\sin hx\} + 2C(0k) = A(k, x),$$

and of

$$2\sum_{1}^{H}\{[C(hk)-C(\bar{h}k)]\sin hx + [S(hk)+S(\bar{h}k)]\cos hx\} + 2S(0k) = B(k, x). \tag{B}$$

$A(k, x)$ and $B(k, x)$ are evaluated separately for each value of k from 1 to K.

The final summation is then given by

$$A(0, x) + \sum_{1}^{K} A(k, x)\cos ky - \sum_{1}^{K} B(k, x)\sin ky.$$

Thus even the general expression can be reduced to the summation of one-dimensional series. In practice, however, this case is not important, as the values of $C(hk)$ and $S(hk)$ are not determinable by experiment. If, however, the projection has a centre of symmetry at the origin (which may be produced by a two-fold axis in the structure perpendicular to the plane of projection)

$$F(hk) = F(\bar{h}\bar{k})$$

and thus the Fs are real.

$$\therefore\quad C(hk) = F(hk) \quad \text{and} \quad S(hk) = 0.$$

In this case

$$A(0, x) = 2\sum_{1}^{H}\{F(h0)\} + F(00),$$

$$A(k, x) = 2\sum_{1}^{H}\{[F(hk)+F(\bar{h}k)]\cos hx\} + 2F(0k),$$

and

$$B(k, x) = 2\sum_{1}^{H}\{[F(hk)-F(\bar{h}k)]\sin hx\}.$$

The projection may have other symmetries which involve relationships between $F(hk)$ and $F(\bar{h}k)$. In such cases the summation is even simpler.

§ 3. PRACTICAL DETAILS

Derivation of numbers. The complete equipment as prepared by the authors consists of 2079 cosine strips and 1980 sine strips. The cosine strips have index-values 0 to 20 inclusive, and the sine strips 1 to 20 inclusive. For each index we have strips of amplitudes $\overline{99}$ to 99. The functions are plotted at intervals of 6° so that the strip corresponding to $A\sin hx$, for example, has printed on it the value of $A\sin(2\pi nh/60)$, correct to the nearest whole number, where n has values from 0 to 15. Each strip has the corresponding negative function on the back. As an example the sine strip for index 3 and amplitude 99 is:

99 S 3	0	31	58	80	94	99	94	80	58	31	0	$\overline{31}$	$\overline{58}$	$\overline{80}$	$\overline{94}$	$\overline{99}$

The strips are cut from a number of tables, each table having one index of cosine or sine with the amplitudes in successive rows.

The different tables are printed from the same columns of type merely arranged in different ways. For example, if the columns for sine 1 are numbered 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, then for sine 2 we have the arrangement of columns 0, 2, 4, 6, 8, 10, 12, 14, 14, 12, 10, 8, 6, 4, 2, 0; and for cosine 6 we have the order: 15, 9, 3, $\bar{3}$, $\bar{9}$, $\overline{15}$, $\bar{9}$, $\bar{3}$, 3, 9, 15, 9, 3, $\bar{3}$, $\bar{9}$, $\overline{15}$, the superior negative signs indicating that all the numbers in the column are negative instead of positive.

The area of summation. If we deal with crystals for which the projection possesses a centre of symmetry it is necessary to obtain the projection for only half of the unit cell. Sometimes the projection will have other symmetry elements which will still further reduce the area to be evaluated. The largest area which will have to be dealt with is given by the conditions that one parameter must go from 0 to 0·50 and the other from 0 to 1·00. This area can, however, easily be derived from the area 0 to 0·25 by 0 to 0·25 which is the area covered directly by the strips. The general rule which enables this extension of area to be effected is that in carrying out any of the one-dimensional summations even indices and odd indices must be kept separate. If, for example, we are summing cosine terms, we see that $\cos hx$ is symmetrical about $x=0{\cdot}25$ when h is even, and is antisymmetrical about $x=0{\cdot}25$ when h is odd. Thus, if in the summation we keep separate the terms with h even and h odd, we have only to add and subtract the two sets of totals in order to obtain the sums for $x=0$ to 0·25 and $x=0{\cdot}50$ to 0·25, respectively. In the case of sine terms we sum first for the planes with h odd, and then for those with h even. Sum and difference then give $x=0$ to 0·25 and $x=0{\cdot}50$ to 0·25, respectively. These ways of extending the range are illustrated in table 3, where they are applied to the summations of $\cos ky$ and $\sin ky$.

To extend the range of a parameter to 0·50 to 1·00 we notice that all the cosine terms are symmetrical about 0·50 whilst all the sine terms are antisymmetrical about this point. We therefore have to subtract sine terms from cosine terms to give the range 0 to 0·50 and to add them to give the range 1·00 to 0·50. In this way we derive the whole of the projection. The process is illustrated in table 4.

Storage of strips. The strips are kept in two similar wooden boxes(7), one for cosine strips and one for sines. All the strips of one index are kept in one compartment, the partitions between the compartments being made of aluminium. The sloping sides of the boxes ensure that on removal of one strip from a compartment its place shall be left open for its reinsertion. If desired the boxes may be made portable by fitting them with lids, some device being used to clamp the strips.

§ 4. PRECAUTIONS AGAINST ERRORS

Mistakes in the use of the strips can arise either from selection of the wrong strip or from errors in addition of the numbers. The former can be guarded against by a simple check. The strips are removed from the boxes by selecting the index, and then the amplitude required for that index, and so on, the order of consideration being thus index, amplitude, index, amplitude, and so on. They should be checked by a glance down the index column, which will in general be 1, 3, 5, 7,... or 0, 2, 4, 6,..., and then by looking down the amplitude column, with special attention to signs. Mistakes in adding will be guarded against by the repetition of each addition. Especial care should be taken over the preliminary tables as an error here will run through a large part of the work.

If desired a complete check could be made by carrying out the summation the other way round. If for example the synthesis was done by first collecting the *F*s with the same *h* in the preliminary tables and multiplying by the cos *ky* functions, it could be repeated by collecting first the *F*s with the same *k* and multiplying by the cos *hx* functions. Usually, however, it will be enough to work out one line of the synthesis in this way.

§ 5. EXAMPLE OF THE USE OF THE STRIPS

In order to compare the procedure with that of the method previously described [(2)] the same example will be used.

Table 1 shows the values of *F* (*hk*) for $CuSO_4 . 5H_2O$, which has only centro-symmetry. It will be observed that the maximum value of *h* is 8, whereas that of *k* is 13. It is therefore advisable to sum first with respect to *k*, so that the largest summations are confined to the shorter preliminary tables. Moreover, since the maximum value of *h* is only 8, the *h* indices may be multiplied by 2 in order to double the interval of division along the corresponding edge of the projection.

Table 1. Values of $F(hk0)$

$F(hk0) = F(\bar{h}\bar{k}0)$

											h							
		$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4	5	6	7	8
	0	8	11	12	0	28	0	33	26	129	26	33	0	28	0	12	11	8
	1		11	0	20	0	21	$\overline{18}$	30	0	18	10	19	$\overline{10}$	0	0	0	
	2		0	0	0	0	$\overline{21}$	0	$\overline{17}$	12	$\overline{32}$	17	$\bar{7}$	10	0	9	0	
	3		0	0	18	7	26	$\overline{20}$	23	11	50	17	18	7	16	6	8	
	4		0	18	13	26	8	27	17	0	0	17	10	8	0	10		
k	5		0	0	0	0	12	0	0	$\overline{14}$	11	$\overline{15}$	0	$\overline{10}$	0	0		
	6		0	0	0	7	0	16	0	12	14	15	0	9	0	0		
	7		7	0	13	9	19	15	21	15	18	0	19	7	15			
	8		0	10	0	0	0	16	$\bar{8}$	12	0	11	0	0	0			
	9			0	0	0	0	$\overline{11}$	0	0	0	0	7	0				
	10			8	0	12	0	14	7	16	0	10	0	12				
	11				13	0	12	0	17	0	8	0	7					
	12				0	0	0	0	0	0	0	0						
	13					0	0	0	11	0	7							

It is convenient next to prepare tables 2*a* and 2*b* which give the values of $F(hk)+F(\bar{h}k)$ and $F(hk)-F(\bar{h}k)$ respectively. Where one index is zero the values of $F(h\text{o})$ and $F(\text{o}k)$ only are used, and the value of $F(\text{oo})$ is divided by 2. Comparison with the general formula will show that this is equivalent to dividing the whole series by 2, the smaller numbers making the subsequent additions less laborious. This process will be different in cases of higher symmetry for which, for example $F(hk)=F(\bar{h}k)$, when the series may be divided by 4. Then the numbers in table 2*b* will be zero, and in table 2*a* will be the single F values, except that $F(h\text{o})$ and $F(\text{o}k)$ will be divided by 2, and $F(\text{oo})$ by 4. The process is most easily visualized in terms of the reciprocal lattice$^{(6)}$. To each point (h, k) of the *ab* section of the lattice is attached a weight $F(hk)$. If $F(hk)=F(\bar{h}k)$ each weight $F(hk)$ occurs four times, $F(\text{o}k)$ and $F(h\text{o})$ twice, and $F(\text{oo})$ once.

Table 2*a*

Values of $F(hk\text{o})+F(\bar{h}k\text{o})$.

					2*h*					
		0	2	4	6	8	10	12	14	16
	0	65	26	33	*0*	28	0	12	11	8
	2	12	$\overline{49}$	17	$\overline{\mathit{28}}$	10	0	9	0	
	4	0	17	44	*18*	34	13	28	0	
k	6	12	14	31	*0*	16	0	0	0	
	8	12	$\overline{8}$	27	*0*	0	0	10	0	
	10	16	7	24	*0*	24	0	8		
	12	0	0	0	*0*	0	0			
	1	0	48	$\overline{8}$	*40*	$\overline{10}$	20	0	11	
	3	11	73	$\overline{3}$	*44*	14	34	6	8	
	5	$\overline{14}$	11	$\overline{15}$	*12*	$\overline{10}$	0	0	0	
k	7	15	39	15	*38*	16	28	0	7	
	9	0	0	$\overline{11}$	*7*	0	0	0		
	11	0	25	0	*19*	0	13			
	13	0	18	0	*0*	0				

Table 2*b*

Values of $F(hk\text{o})-F(\bar{h}k\text{o})$

					2*h*					
		0	2	4	6	8	10	12	14	16
	0	0	0	0	*0*	0	0	0	0	0
	2	0	$\overline{15}$	17	*14*	10	0	9	0	
	4	0	$\overline{17}$	$\overline{10}$	*2*	$\overline{18}$	$\overline{13}$	$\overline{8}$	0	
k	6	0	14	$\overline{1}$	*0*	2	0	0	0	
	8	0	8	$\overline{5}$	*0*	0	0	$\overline{10}$	0	
	10	0	$\overline{7}$	$\overline{4}$	*0*	0	0	$\overline{8}$		
	12	0	0	0	*0*	0	0			
	1	0	$\overline{12}$	28	$\overline{\mathit{2}}$	$\overline{10}$	$\overline{20}$	0	$\overline{11}$	
	3	0	27	37	$\overline{\mathit{8}}$	0	$\overline{2}$	6	8	
	5	0	11	$\overline{15}$	$\overline{\mathit{12}}$	$\overline{10}$	0	0	0	
k	7	0	$\overline{3}$	$\overline{15}$	*0*	$\overline{2}$	2	0	$\overline{7}$	
	9	0	0	11	*7*	0	0	0		
	11	0	$\overline{9}$	0	$\overline{\mathit{5}}$	0	$\overline{13}$			
	13	0	4	0	*0*	0				

Tables 3*a* and 3*b* are the parts of the preliminary tables for which $2h=6$, and in these tables the actual strips used are depicted. Of course, only the totals would be written down. The amplitude columns of the strips used in tables 3 correspond with columns (shown in italics) in table 2*a* and 2*b*. The results of tables 3*a*, 3*b* are given in the rows designated "difference" and "sum", which give the totals corresponding to the two ranges of y, 0 to 15/60, and 30/60 to 15/60.

The results of all the preliminary tables for the different values of h are collected in a table 3*c*, not shown. This table then serves for the construction of the final tables, of which table 4 shows the portion for $y=7/60$. Each set of strips has its amplitude column taken from table 3*c*, and the difference and sum of the cosine and sine parts gives a line of the final totals.

Table 3*a*

Evaluation of $\frac{1}{2}A\,(2h, y)$ for $2h = 6, = \sum_{1}^{K} [F(6k) + F(\bar{6}k)] \cos ky + F(60)$

y (60ths)

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\bar{28}$ C 2	$\bar{28}$	$\bar{27}$	$\bar{26}$	$\bar{23}$	$\bar{19}$	$\bar{14}$	$\bar{9}$	$\bar{3}$	3	9	14	19	23	26	27	28
18 C 4	18	16	12	6	$\bar{2}$	$\bar{9}$	$\bar{15}$	$\bar{18}$	$\bar{18}$	$\bar{15}$	$\bar{9}$	$\bar{2}$	6	12	16	18
	$\bar{10}$	$\bar{11}$	$\bar{14}$	$\bar{17}$	$\bar{21}$	$\bar{23}$	$\bar{24}$	$\bar{21}$	$\bar{15}$	$\bar{6}$	5	17	29	38	43	46
40 C 1	40	40	39	38	37	35	32	30	27	24	20	16	12	8	4	0
44 C 3	44	42	36	26	14	0	$\bar{14}$	$\bar{26}$	$\bar{36}$	$\bar{42}$	$\bar{44}$	$\bar{42}$	$\bar{36}$	$\bar{26}$	$\bar{14}$	0
12 C 5	12	10	6	0	$\bar{6}$	$\bar{10}$	$\bar{12}$	$\bar{10}$	$\bar{6}$	0	6	10	12	10	6	0
38 C 7	38	28	4	$\bar{22}$	$\bar{37}$	$\bar{33}$	$\bar{12}$	15	35	36	19	$\bar{8}$	$\bar{31}$	$\bar{38}$	$\bar{25}$	0
7 C 9	7	4	$\bar{2}$	$\bar{7}$	$\bar{6}$	0	6	7	2	$\bar{4}$	$\bar{7}$	$\bar{4}$	2	7	6	0
19 C 11	19	8	$\bar{13}$	$\bar{18}$	$\bar{2}$	16	15	$\bar{4}$	$\bar{19}$	$\bar{11}$	9	19	6	$\bar{14}$	$\bar{17}$	0
	160	132	70	17	0	8	15	12	3	3	3	$\bar{9}$	$\bar{35}$	$\bar{53}$	$\bar{40}$	0
Difference	150	121	56	0	$\bar{21}$	$\bar{15}$	$\bar{9}$	$\bar{9}$	$\bar{12}$	$\bar{3}$	8	8	$\bar{6}$	$\bar{15}$	3	46
Sum	$\bar{170}$	$\bar{143}$	$\bar{84}$	$\bar{34}$	$\bar{21}$	$\bar{31}$	$\bar{39}$	$\bar{33}$	$\bar{18}$	$\bar{9}$	2	26	64	91	83	
	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15

y (60ths)

Table 3*b*

Evaluation of $\frac{1}{2}B\,(2h, y)$ for $2h = 6, = \sum_{1}^{K} [F(6k) - F(\bar{6}k)] \sin ky$.

y (60ths)

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\bar{2}$ S 1	0	0	0	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{2}$
$\bar{8}$ S 3	0	$\bar{2}$	$\bar{5}$	$\bar{6}$	$\bar{8}$	$\bar{8}$	$\bar{8}$	$\bar{6}$	$\bar{5}$	$\bar{2}$	0	2	5	6	8	8
$\bar{12}$ S 5	0	$\bar{6}$	$\bar{10}$	$\bar{12}$	$\bar{10}$	$\bar{6}$	0	6	10	12	10	6	0	$\bar{6}$	$\bar{10}$	$\bar{12}$
7 S 9	0	6	7	2	$\bar{4}$	$\bar{7}$	$\bar{4}$	2	7	6	0	$\bar{6}$	$\bar{7}$	$\bar{2}$	4	7
$\bar{5}$ S 11	0	$\bar{5}$	$\bar{4}$	2	5	2	$\bar{3}$	$\bar{5}$	$\bar{1}$	4	4	$\bar{1}$	$\bar{5}$	$\bar{3}$	2	5
	0	$\bar{7}$	$\bar{12}$	$\bar{15}$	$\bar{18}$	$\bar{20}$	$\bar{16}$	$\bar{4}$	10	18	12	$\bar{1}$	$\bar{9}$	$\bar{7}$	2	6
14 S 2	0	3	6	8	10	12	13	14	14	13	12	10	8	6	3	0
2 S 4	0	1	1	2	2	2	1	0	0	$\bar{1}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{1}$	$\bar{1}$	0
	0	4	7	10	12	14	14	14	14	12	10	8	6	5	2	0
Difference	0	$\bar{3}$	$\bar{5}$	$\bar{5}$	$\bar{6}$	$\bar{6}$	$\bar{2}$	10	24	30	22	7	$\bar{3}$	$\bar{2}$	4	6
Sum	0	$\bar{11}$	$\bar{19}$	$\bar{25}$	$\bar{30}$	$\bar{34}$	$\bar{30}$	$\bar{18}$	$\bar{4}$	6	2	$\bar{9}$	$\bar{15}$	$\bar{12}$	0	
	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15

y (60ths)

Table 4. Final summations for $y = 7/60$

$$A(0, 7/60) + \sum_{1}^{H} A(h, 7/60)\cos hx - \sum_{1}^{H} B(h, 7/60)\sin hx$$

x (30ths)

	0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
93 *C* 0	93	93	93	93	93	93	93	93	93	93	93	93	93	93	93	9
$\overline{26}$ *C* 2	$\overline{26}$	$\overline{25}$	$\overline{24}$	$\overline{21}$	$\overline{17}$	$\overline{13}$	$\bar{8}$	$\bar{3}$	3	8	13	17	21	24	25	2
24 *C* 4	24	22	16	7	$\bar{3}$	$\overline{12}$	$\overline{19}$	$\overline{23}$	$\overline{23}$	$\overline{19}$	$\overline{12}$	$\bar{3}$	7	16	22	2
$\bar{9}$ *C* 6	$\bar{9}$	$\bar{7}$	$\bar{3}$	3	7	9	7	3	$\bar{3}$	$\bar{7}$	$\bar{9}$	$\bar{7}$	$\bar{3}$	3	7	
4 *C* 8	4	3	0	$\bar{3}$	$\bar{4}$	$\bar{2}$	1	4	4	1	$\bar{2}$	$\bar{4}$	$\bar{3}$	0	3	
$\overline{10}$ *C* 10	$\overline{10}$	$\bar{5}$	5	10	5	$\bar{5}$	$\overline{10}$	$\bar{5}$	5	10	5	$\bar{5}$	$\overline{10}$	$\bar{5}$	5	1
$\bar{5}$ *C* 12	$\bar{5}$	$\bar{2}$	4	4	$\bar{2}$	$\bar{5}$	$\bar{2}$	4	4	$\bar{2}$	$\bar{5}$	$\bar{2}$	4	4	$\bar{2}$	
17 *C* 14	17	2	$\overline{17}$	$\bar{5}$	16	8	$\overline{14}$	$\overline{11}$	11	14	$\bar{8}$	$\overline{16}$	5	17	$\bar{2}$	$\bar{1}$
8 *C* 16	8	$\bar{1}$	$\bar{8}$	2	7	$\bar{4}$	$\bar{6}$	5	5	$\bar{6}$	$\bar{4}$	7	2	$\bar{8}$	$\bar{1}$	
	96	80	66	90	102	69	42	67	99	92	71	80	116	144	150	15
$\overline{39}$ *S* 2	0	$\bar{8}$	$\overline{16}$	$\overline{23}$	$\overline{29}$	$\overline{34}$	$\overline{37}$	$\overline{39}$	$\overline{39}$	$\overline{37}$	$\overline{34}$	$\overline{29}$	$\overline{23}$	$\overline{16}$	$\bar{8}$	
88 *S* 4	0	36	65	84	88	76	52	18	$\overline{18}$	$\overline{52}$	$\overline{76}$	$\overline{88}$	$\overline{84}$	$\overline{65}$	$\overline{36}$	
10 *S* 6	0	6	10	10	6	0	$\bar{6}$	$\overline{10}$	$\overline{10}$	$\bar{6}$	0	6	10	10	6	
4 *S* 8	0	3	4	2	$\bar{1}$	$\bar{3}$	$\bar{4}$	$\bar{2}$	2	4	3	1	$\bar{2}$	$\bar{4}$	$\bar{3}$	
$\overline{33}$ *S* 10	0	$\overline{29}$	$\overline{29}$	0	29	29	0	$\overline{29}$	$\overline{29}$	0	29	29	0	$\overline{29}$	$\overline{29}$	
9 *S* 12	0	9	5	$\bar{5}$	$\bar{9}$	0	9	5	$\bar{5}$	$\bar{9}$	0	9	5	$\bar{5}$	$\bar{9}$	
6 *S* 14	0	6	1	$\bar{6}$	$\bar{2}$	5	4	$\bar{4}$	$\bar{4}$	4	5	$\bar{2}$	$\bar{6}$	1	6	
	0	23	40	62	82	73	18	$\overline{61}$	$\overline{103}$	$\overline{96}$	$\overline{73}$	$\overline{74}$	$\overline{100}$	$\overline{108}$	$\overline{73}$	
Difference	96	57	26	28	20	$\bar{4}$	24	128	202	188	144	154	216	252	223	
Sum	96	103	106	152	184	142	60	6	$\bar{4}$	$\bar{4}$	$\bar{2}$	6	16	36	77	152
	30	*29*	*28*	*27*	*26*	*25*	*24*	*23*	*22*	*21*	*20*	*19*	*18*	*17*	*16*	*15*

x (30ths)

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538.22 : 546.76

THE MAGNETIC PROPERTIES OF CHROMIUM

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ABSTRACT. Pure chromium has been prepared from chromium amalgam and its magnetic susceptibility has been studied over the temperature range 90 to 620° K. The mass susceptibility is practically constant over this range, the slight departures from constancy being partially explainable by the effects of thermal expansion on the experimental results. The mean susceptibility is $3\cdot08\times10^{-6}$ e.m.u. per gram at room temperature. The effects of impurities on the magnetic behaviour of chromium, which are very pronounced in the case of samples prepared at lower temperatures, are considered in detail, and the thermal and magnetic data for this element are discussed on the basis of modern theories of paramagnetism of metals.

§ 1. INTRODUCTION

CHROMIUM belongs to the first transition group of elements and its magnetic properties are, therefore, of considerable interest; yet a survey of the literature shows that they have been somewhat inadequately investigated. For example, the value of the susceptibility per gram given in the *International Critical Tables* is $3\cdot7\times10^{-6}$ c.c.s. units, derived from the work of Honda(1). An examination of the curves of susceptibility plotted against H shows conclusively that the materials used were markedly ferromagnetic, and indeed the chemical analysis given in Honda's paper includes the statement that the chromium used by him contained 2 per cent of iron. This is extraordinarily large and is probably an overestimate in view of the properties we have found specimens of chromium to possess in the present investigations. Again, in Owen's work(2) the amount of iron stated to be contained in his specimen of chromium was 5·3 parts per 1000, and the value of χ is given as $3\cdot175\times10^{-6}$ in a field of 26,000 oersteds, and $2\cdot87\times10^{-6}$ when extrapolated to the value in an infinitely large field. We must conclude, then, that pure chromium has so far not been investigated. This is a little surprising in view of the manner in which chromium is so readily produced in large-scale electrolytic processes for use in commerce, but it must be remembered that such preparations contain large amounts of occluded gases, notably oxygen and hydrogen, which are inseparable from the method of manufacture, and no particular care is exercised to avoid the presence of traces of iron.

In some recent work, Bates and Reddi Pantulu(3) examined the properties of amorphous manganese and showed that this element could be prepared in a non-ferromagnetic state in spite of its well-known tendency to combine with other elements to form ferromagnetic compounds. It therefore seemed to us to be of interest to prepare specimens of pure chromium by the same method for a survey of it magnetic properties. It is generally assumed that the preparation of chromium amalgam is much easier than the preparation of manganese amalgam, but in ou work we found that the former preparation was attended with considerable difficulties, although we eventually succeeded in preparing specimens of the material which we regarded as satisfactory for the purposes of our investigations.

§2. PREPARATION OF MATERIAL

Concentrated solutions of chromic sulphate, $Cr_2(SO_4)_3.7H_2O$, were prepared from the salt obtained from Hopkins and Williams, or from green flakes of specially pure chromium sulphate obtained from Merck, or from the violet powder supplied by British Drug Houses Ltd.; the first product was found the best for our purposes. To each litre of solution 7 cm.^{3} of sulphuric acid was added. The solution was then electrolyzed, a platinum plate being used as anode and a pool of mercury as cathode. During the course of electrolysis the strength of the solution was maintained by the periodic addition of chromic sulphate crystals. Currents of approximately 14 A., corresponding to a current density of 1·1 A./cm.^{2} at the cathode, were usually passed for some 100 minutes. These produced satisfactory amalgams, but it was found that higher current-densities produced a flaking of the amalgam surface or a partial breakdown of the amalgam, apparently with the deposition of crystalline chromium, in addition to excessive heating of the solution. The latter was contained in a thin-walled glass vessel placed in a container through which cold water circulated.

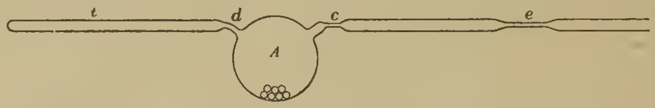

Figure 1. Apparatus for distillation of chromium amalgam.

The electrolysis was accompanied by the copious evolution of hydrogen, and slight stirring of the mercury surface was desirable. The amalgams were rather thin and quite unlike the pasty type obtained with manganese. They did, however, contain some lumps rich in chromium which were easily dispersed throughout the main body of the liquid. Now, one of the main difficulties which accompanied the handling of the amalgam lay in the fact that chromium amalgam is unstable in the presence of non-acidulated water; consequently it could not be washed in the usual manner, and it had to be washed several times with absolute alcohol for the best results, although preliminary washing with water and later washing with absolute alcohol was also tried in the case of a few preparations.

The amalgam was introduced into the bulb of the pyrex glass apparatus shown in figure 1, which is somewhat similar to that employed in the earlier work, but the present design was made for the more efficient handling of large volumes of amalgam and their subsequent treatment. The vessel was first evacuated through a short piece of new rubber pressure tubing which was then clipped, detached from the pump, and provided with a funnel whose exit tube was suitably narrowed. The funnel was lined with filter paper, and when the amalgam was placed in it, any residual alcohol ir slight impurity formed by washing came to the surface. The clip was opened and he amalgam stirred slowly as it trickled into the apparatus, impure portions being ffectively shut out by closing the clip at the proper time. All these operations were arried out as quickly as possible, and, in our view, the success of the preparation epends upon the rapidity with which they are performed. The apparatus was then peedily connected to a Hyvac pump through a cooled vessel, in which mercury ould condense, and drying tubes; liquid-air traps and a mercury-vapour pump ere later brought into use.

The mercury was at first boiled off fairly rapidly, for in this way any film of oxide n its surface was carried over into the condenser. In the early experiments the emperature was not raised above 400° C., and when the removal of mercury had een as far as possible completed the glass apparatus was sealed at the constriction *c*, igure 1. The bulb *A* now contained the several pyrex glass beads and a mass of hromium. This mass was exceedingly hard and its pulverization with the glass eads was practically impossible; the bulb *A* was therefore broken and the substance readily powdered with a glass rod and introduced into a new apparatus similar to hat of figure 1. This was evacuated with a mercury-vapour pump and heated to about 400° C. for about three hours. The powder was then forced into the tube *t* through the constriction *d* which was afterwards sealed. This was the mode of preparation of specimens similar to no. I. It should be mentioned that when the bulb *A* was broken, some slight pyrophoric action between the air and the traces of powdered chromium inside occurred, but there was no trace of such action with the main mass of the specimen which we used in our measurements. Measurements made with specimens like no. I showed that the temperature 400° C. was not sufficiently high to remove all traces of mercury and hydrogen occluded during electrolysis. The effects of such occlusions will be described below. In later experiments we therefore raised the temperature of the bulb *A* and its contents to 500° C. and maintained it for four hours. It was also found that when the temperature was raised to 500° C. the chromium yield was easily powdered *in situ* without the necessity of breaking the bulb *A*. In this way specimens like no. IX were prepared, and we are therefore disposed to regard such specimens as the purest obtained. It was usually found convenient to seal the apparatus at the constriction *e*, and then to powder the chromium. The apparatus was next connected to the pumping system by slipping rubber pressure tubing over the seal at *e*, and, when the pumps were effectively running, connexion was made to the bulb *A* by breaking the glass at a file mark previously made near the seal *e*. The temperature of the powder was then raised, and it was found, in agreement with the work of Makariewa and Birükoff(4), that hydrogen was copiously evolved in the region of 580° C. This was the treatment given to the specimen no. IX, which was maintained at the highest temperature permissible with pyrex glass under atmospheric pressure until no more evolution of gas could be detected by means of a vacuum tester. Specimen no. IX may be regarded as reasonably free of mercury, hydrogen and oxide, and we do not think it possible with present technique to obtain a much purer specimen with this temperature treatment.

§3. MAGNETIC MEASUREMENTS

H

The sealed tube t containing the specimen was provided with hooks an suspended vertically from one arm of a sensitive chemical balance and measurement were made by the Gouy method. To the lower end of the tube t was attached a evacuated pyrex tube of the same dimensions, in the manner described in th previous paper by Bates and Reddi Pantulu(3). The lower end of the specimen wa thus placed in a uniform magnetic field H while its upper end was in a practicall field-free space when the electromagnet was excited. The pull exerted on th specimen by the magnetic forces was then given by

$$mg = \tfrac{1}{2}k\alpha H^2,$$

α, m

where α is the area of cross-section of the tube t, and m the difference between th masses in the pan of the balance when the field was off and when it was on. Correc tions for the magnetic effect of the air surrounding the suspended system and fo the glass were avoided by the use of the lower evacuated tube.

k

The quantity k in the above expression represents the volume susceptibility o chromium as packed in the tube; hence, to find the mass susceptibility the packing density was found later. The absolute accuracy of the results depends on the uniformity of the cross-section α; the tubes were selected with care and measured prior to use, the value of α being finally obtained by direct measurement afte removal of the chromium. Determinations of k were made over the range o temperature −183 to 350° C. For the high-temperature measurements the furnac arrangement used by Bates and Reddi Pantulu was employed, but the work was greatly facilitated by the addition of a special water jacket placed between the pole pieces to maintain the latter at a uniform temperature and to stabilize the furnace temperatures. The construction of this water jacket is shown in figure 2. It was made of thin sheet brass soldered to a frame with solid ends, as shown in the left part of the figure. The water was forced to flow evenly through the side wings by a perforated baffle around the middle, indicated by the broken line, so that the whole jacket was maintained at a uniform temperature.

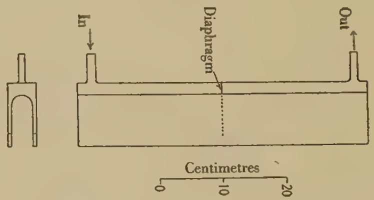

Figure 2. Diagram of water jacket for furnace.

For the measurements at carbon-dioxide and liquid-oxygen temperatures the specimen was suspended inside a copper tube, with a piece of rubber tubing fitted to its upper end and mounted inside a Dewar flask containing carbon dioxide snow or liquid oxygen. In one or two cases the tube was replaced by a very thick copper block which was first cooled by liquid oxygen, after which its temperature rose wly, and at a convenient temperature recorded by a thermocouple a magnetic easurement was taken; this was not really satisfactory and the accuracy of such easurements was not high, but they provided very valuable checks upon the sults obtained at other temperatures.

§4. EXPERIMENTAL RESULTS FOR LOW-TEMPERATURE PREPARATIONS

In view of the foregoing remarks, the results obtained with specimen no. IX will described first. In common with every specimen so far made, this specimen hibited traces of ferromagnetism. Consequently in all our determinations we plied the Owen-Honda correction, using the equation

$$\chi_\infty = \chi_H - 2\sigma/H,^*$$

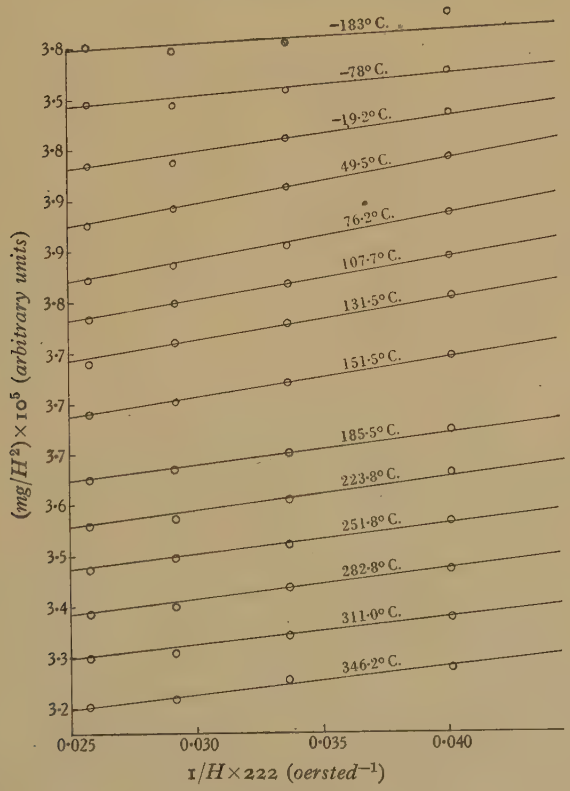

Figure 3. Specimen no. IX. Graphs showing mg/H^2, which is a measure of susceptibility, as a function of $1/H$.

vhere σ is the saturation specific magnetization of the impurity. A typical set of leterminations is shown in figure 3, where the magnetic pull divided by H^2 is plotted

---

* This equation is generally written $\chi_\infty = \chi_H - \sigma/H$, but in this form it can only be used with easurements in which small spherical specimens are placed in a non-uniform field, where $H.dH/dx$ involved. The derivation of the correct formula for use with the Gouy method was first made by ogt(5).

as a function of $1/H$ for a series of different temperatures. The intercept at $1/H=$
gave the true value of the susceptibility of the paramagnetic material. It was not foun
necessary to apply the more complicated form of correction suggested by Vogt(
At the same time it should be pointed out that this assumes that the ferromagnetis
is due to an impurity or rather to a compound of chromium and an impurity, ar
not due to pure chromium; this is a matter which will be discussed further. It i
of course, possible to obtain from the curves shown in figure 3, the magnitude of t
ferromagnetic correction at each temperature.

χ The values of χ, the susceptibility per gram of chromium for specimen no. I
are shown in figure 4, together with the corresponding values of $1/\chi$ and the ferr
magnetic correction 2σ obtained from the lines of figure 3. The value of the ma
susceptibility at the room temperature is $3{\cdot}21 \times 10^{-6}$ at 20° C., which is some 10 p
cent lower than that given by Honda and 10 per cent higher than that given
Owen. It will be observed that with decrease in temperature from 600° K. dow
to the temperature of the room there is a more or less uniform increase of χ. The
then occurs a slight decrease in the susceptibility between room temperature and t
temperature of solid CO_2, after which the susceptibility shows an increase. T
curve of $1/\chi$ against T does not appear to call for special comment. It is obvio
however, that valuable information might be obtained at liquid-hydrogen temper
tures, but these are beyond our present resources. The curve showing the variati
of ferromagnetic correction with temperature is very striking, and there is no dou
whatever of the reality of the maximum there shown.

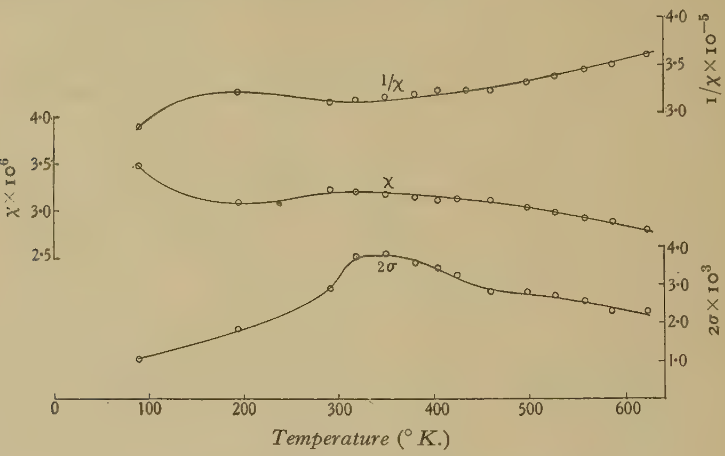

Figure 4. Specimen no. IX. Maximum temperature during preparation, 600° C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

Specimen no. IV was prepared in the same way as no. IX except that the bulb
was accidentally cracked after the chromium had been powdered. The powder w
placed in a tube, evacuated and heated to 620° C. for 4 hours, and then seale
There was, therefore, the possibility that traces of oxygen and nitrogen might ha
had an opportunity of combining with the chromium, although precautions we

aken to evacuate the tube thoroughly before heating it. The curves of χ and $1/\chi$ re shown in figure 5 together with ferromagnetic corrections. There is some slight rregularity in the determinations, due mainly to uncertainty of correction for the erromagnetic impurity, and it is seen that there is again a pronounced change in the aramagnetic properties as the temperature falls from that of the room to that of iquid oxygen, a change much like that found in specimen no. IX, except that there s now no sign of a decrease between +14 and −78° C. The value of the suscepti-bility $3{\cdot}86 \times 10^{-6}$ at room temperature (14° C.), was also rather high.

The preparation of specimen no. I differed from that of no. IX in that occluded gases were not so thoroughly removed. The curves corresponding to figure 3 obtained with this specimen were striking in that they were parallel within the limits of experimental error for temperatures between 350° C. and the room temperature, but the ferromagnetic correction assumed rather large proportions at temperatures below that of the room. This is shown by the ferromagnetic-correction curve of figure 6, where the variation of χ and $1/\chi$ with T for this specimen also are shown. The curve of χ shows a much more pronounced rise than that which occurred in the case of specimen no. IX, and we satisfied ourselves with a copper-block experiment that the shape of the curve given in figure 6 is substantially correct. The $1/\chi$ curve shows a very marked break in the neighbourhood of 0° C. It provides a striking example of what is termed a *droite coudée*(6) or "elbowed curve", and we are tempted to enquire whether such curves really owe their existence to the presence of occluded gases in other experiments in which they have been recorded; we did not obtain such a marked break in any curve for specimens in which the hydrogen was effectively removed. The value of χ at room temperature was $3{\cdot}80 \times 10^{-6}$. The experiments so far described have been confined to specimens of chromium which have never been heated much above 600° C., and for such specimens we conclude that the most reliable value of the susceptibility at room temperature is $3{\cdot}2 \times 10^{-6}$ if they have never

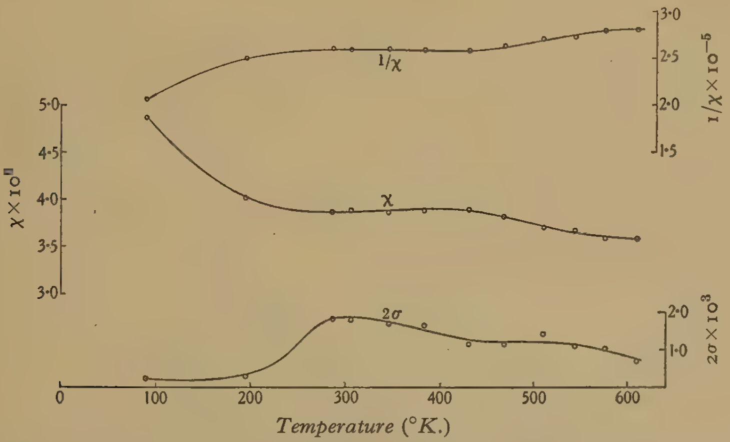

Figure 5. Specimen no. IV. Maximum temperature during preparation, 600 °C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

been in contact with air. It is interesting that we obtained about the same value as those obtained by Honda for our less pure specimens.

The peculiarities of figure 6 are attributed mainly to the effects of traces o mercury occluded in the chromium, which give rise to much uncertainty and irregularity in the determination of the ferromagnetic correction and to the pronounced upper sweep of the $\{\chi, T\}$ curve with its associated elbow. From the othe curves it appears clear that occluded hydrogen causes an increase in the value of the susceptibility, but its effect on the ferromagnetic correction could not be determined with certainty from the above experiments. The peculiar shape of the curves showing ferromagnetic correction against T was at first somewhat disturbing, but similar curves have previously been recorded by Ochsenfeld$^{(7)}$ for alloys of chromium with tellurium giving compounds Cr_3Te, $CrTe$, and $CrTe_2$; these curves are reproduced in figure 7, and it is seen that a pronounced maximum occurs in the case of CrTe. It is unfortunate that Ochsenfeld did not extend his magnetic measurements to temperatures below that of the room. It may be suggested that as oxygen and tellurium are in the same column of the periodic table the ferromagnetism of our specimens may be due to traces of a compound of chromium and oxygen. We felt, however, that it is much more likely to be due to a combination of chromium with hydrogen and this view we think is supported by the experiments described in §5 below.

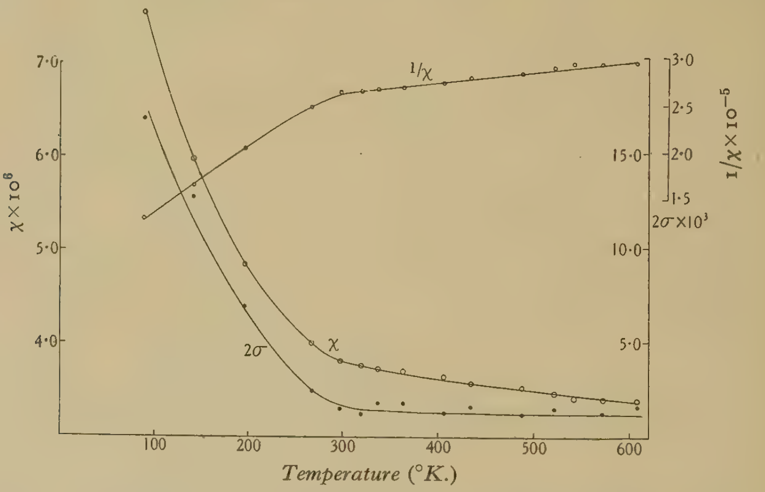

Figure 6. Specimen no. I. Maximum temperature during preparation, 420° C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

The effects of traces of mercury on the properties of chromium were brought out in the study of specimen no. III, which was not heated above 370° C. in the preliminary treatment. Starting at a temperature of −183° C. and proceeding to 350° C., the susceptibility remained practically constant. Yet between 320° C. and 350° C. disturbances became apparent, the first results could not be repeated, and with decrease in temperature from 350° C. down to room temperature a constant increase in susceptibility was recorded; below this the susceptibility somewhat decreased. In these measurements the ferromagnetic correction remained constant and small. The specimen was now heated to 580° C. with the empty end of the tube projecting beyond the furnace. A globule of mercury condensed in this end and was removed by sealing off and detaching a portion of the tube. Magnetic measurements were then reproducible, but the ferromagnetic correction, which was of the type shown in figures 4 and 5, was enormously increased; the maximum value of 2σ, which occurred at approximately 30° C., was $4{\cdot}2 \times 10^{-2}$ per gram. Thus this specimen had associated with it a ferromagnetism at least twenty times as great as that obtained with specimen no. IX in the above experiments, as a result, no doubt, of the replacement of mercury by occluded hydrogen. It was therefore considered essential to evacuate the tube containing the specimen thoroughly during the high-temperature treatments described below, in order to remove all traces of hydrogen and mercury.

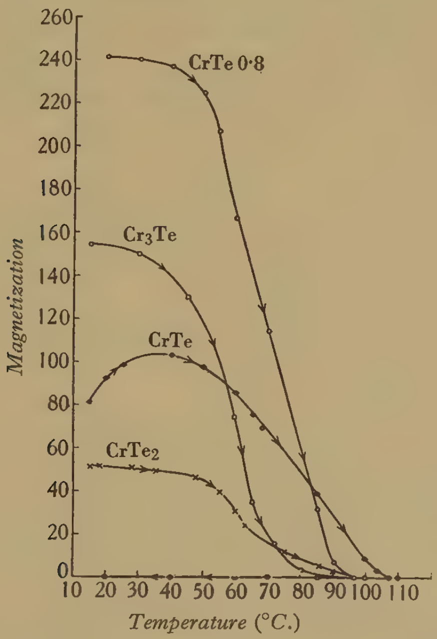

Figure 7. Ochsenfeld's curves showing variation of magnetization with temperature for compounds of chromium and tellurium.

§5. EXPERIMENTAL RESULTS FOR HIGH-TEMPERATURE PREPARATIONS

The material of specimen no. IX was placed in a quartz tube and kept at 800° C. for four hours while the tube was continuously evacuated. The tube was then sealed and allowed to cool slowly to room temperature, and the susceptibility of the material was then determined by the above method; absolute values were not found.

The curve 1 of figure 8 shows the results obtained and there is no doubt that the ferromagnetic correction has enormously increased. The same tube was replaced in the furnace and maintained at a temperature of 1000° C. for two hours, further evacuation now being impossible. After cooling slowly the susceptibility was redetermined and curve 2 of figure 8 shows that the ferromagnetic correction had decreased to a remarkable extent; this decrease became even more marked when the specimen was heated to 1200° C. for about two hours, and curve 3 was found. The specimen now had the appearance of a sintered rod, and on breaking it up a bright grey powder—a pleasing contrast with our former black specimens—was obtained. The powder was placed in a pyrex glass tube, evacuated and heated to 450° C., and after it had been tempered for nine hours at 350° C., susceptibility measurements were made in the usual way. The relevant graphs of χ_H against $1/H$ are given in figure 9*a*.

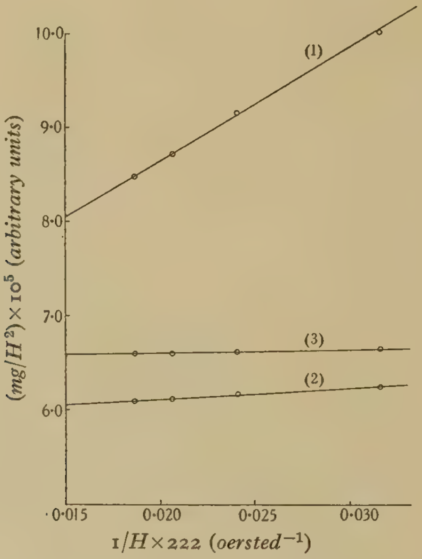

Figure 8. Specimen no. IX after high-temperature treatment. Graphs of mg/H^2, which is a measure of susceptibility, as a function of $1/H$, to show magnitude of ferromagnetic correction. Curve (1), after heating to 800° C. for four hours. Curve (2), after further heating to 1000° C. for two hours. Curve (3), after further heating to 1200° C. for two hours.

A most interesting feature of the behaviour of the specimen was that the ferromagnetic correction 2σ was much smaller and practically constant within the limits of experimental error for all temperatures between $-183°$ C. and $+350°$ C., so that we feel justified in regarding it as due entirely to iron, presumably contained originally in the chromic sulphate and introduced by the electrolysis. It is commonly supposed that it is difficult to introduce iron into mercury, but that is not our experience; in any case the presence of iron to the extent of about two parts in one million of chromium would be sufficient to account for the results now described. It is considered that an X-ray examination of the material of no. IX before and after high-temperature treatment should be of interest, and this will shortly be undertaken.

The curve showing $1/\chi$ against T, figure 9*b*, curve 2, indicates that over a range of temperature from about 35° C. to 350° C. the susceptibility obeys a Curie-Weiss relation of the form

$$\chi = C/T + \Delta$$
$$= \frac{2{\cdot}254 \times 10^{-2}}{T + 6650}.$$

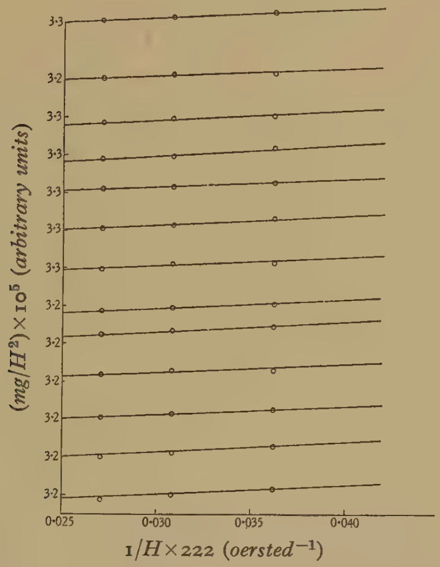

Figure 9*a*. Specimen no. IX after final high-temperature treatment. Graphs showing mg/H^2, which is a measure of susceptibility, as a function of $1/H$.

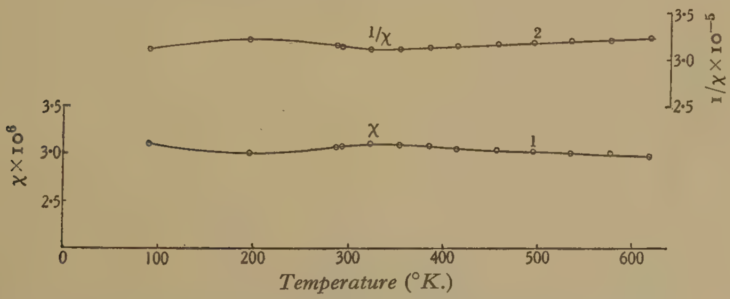

Figure 9*b*. Specimen no. IX. Final results after high-temperature treatment (at 1200° C.). Graphs of χ and $1/\chi$ as functions of temperature.

Below 35° C. the susceptibility shows a rather peculiar fall which may be due to a change in structure, or possibly to an imperfect correction for the ferromagnetism of the specimen, but the latter error is unlikely. Our final result is that susceptibility of the purest chromium so far obtained is $3{\cdot}08 \times 10^{-6}$ e.m.u. per gram or $160{\cdot}3 \times 10^{-6}$ per gram-atom at 20° C. uncorrected for diamagnetism of the core. The accuracy of this absolute value was limited by the accuracy with which the packing density could be found. To provide the usual basis of discussion, the final experimental values of χ shown in figure 9*b*, curve 1, were corrected for the diamagnetism of the core of the chromium atom by the addition of $0{\cdot}127\times10^{-6}$ e.m.u. per gram(8), and the reciprocals of these corrected values are given in curve 2 of figure 9*b*.

To facilitate discussion the treatment and properties of the several specimens are summarized in table 1.

Table 1

Specimen	Treatment	$\chi_{15}\times10^6$	Curve	Remarks
I	Maximum temperature 400° C.	3·88	Fig. 6	Contained traces of mercury and hydrogen. Large ferromagnetic correction of peculiar type (1)
III	Maximum temperature 370° C.	(Not reproducible)	—	Ferromagnetic correction constant and small
	Heated to 580° C. in evacuated sealed tube	4·78	—	Large ferromagnetic correction with maximum at about 40° C.
IV	Maximum temperature about 600° C.	3·86	Fig. 5 (Fig. 3)	Contained hydrogen. Ferromagnetic correction with maximum value at about 40° C. type (2)
IX	Maximum temperature about 600° C.; specimen completely prepared *in vacuo*	3·18	Fig. 4	Contained hydrogen only. Ferromagnetic correc- of type (2) with maximum at about 60° C.
	Specimen no. IX heated to 800° C. in evacuated quartz tube, and, after sealing, heated to 1200° C.; finally powdered, transferred to a pyrex tube, which was evacuated and sealed	3·06	Fig. 8, (Fig. 9*a* and 9*b*)	Free from hydrogen and mercury. Ferromagnetic correction small and constant over wide temperature range

§6. DISCUSSION OF RESULTS

The value of Δ for chromium is considerably higher than that obtained by Bates and Reddi Pantulu for manganese. To some extent it is dependent on the value assumed for the diamagnetism of the atomic core, for if we take no account of this we find the Curie constant and Δ to be respectively $1{\cdot}928\times10^{-2}$ and 5870. On the other hand, if we take the higher value 17×10^{-6} e.m.u. per gram-atom, assumed by Sommerfeld and Bethe(9) for the diamagnetism of the core, we find $2{\cdot}623\times10^{-2}$ and 7310 respectively. However, as the representation $\chi=C/T+\Delta$ is purely formal, it need not be discussed further.

Now, it has been assumed in the above work that no changes occurred in the packing density of the specimen or in the area of cross section of the tube. Actually, s the temperature of the specimen is raised the material must expand and the packing density be decreased. Disch[(10)] has measured the coefficient of linear expansion of chromium over a wide range of temperature, and his results are given in table 2.

Table 2

Temperature, T	-78	100	200	300	400	500	°C.
Mean coefficient of expansion $\times 10^5$, between 0° and $T°$	0·73	0·84	0·875	0·91	0·94	0·97	deg. $^{-1}$

From these figures we should expect the observed volume susceptibility to increase with fall in temperature and the increase to become more pronounced below 0° C. However, Disch mentions the interesting point that while chromium contracts on cooling until the temperature reaches about $-183°$ C. it expands on further cooling to $-190°$ C. Thus while the contraction per metre between $+20$ and $-183°$ C. was 1·25 mm., that between $+20$ and $-190°$ C. was only 1·00 mm. Disch states that the latter values are not accurate, for the chromium surface became deformed at liquid-air temperatures and precise measurements by the Fizeau interference method were impossible. The expansion and magnetic data appear to be in close accord, except that the magnetic measurements indicate that the expansion on cooling begins before $-183°$ C. is reached.

The thermal expansion of chromium is also of interest in connexion with the special features of the curves of figures 4, 5 and 6, for it is concluded that the presence of hydrogen has a pronounced influence in the region where anomalous expansion is found. This is, of course, in agreement with the well-known influence of hydrogen on the magnetic properties of iron[(11)]. It may safely be assumed that the hydrogen makes possible an exchange interaction between the electrons responsible for the magnetic properties of chromium, and so accounts for the observed ferromagnetism and the increased paramagnetism of the specimen and its pronounced temperature changes.

The expansion makes somewhat uncertain the comparison of our experimental results with those expected on the theory of paramagnetism developed by Pauli[(12)] and by Frenkel[(13)], and discussed by Sommerfeld and Bethe[(8)] and in considerable detail by Stoner[(14)]. This theory gives the following expression for $(\chi_A)_e$, the resultant paramagnetic susceptibility of the quasi-free electrons in one gram-atom of the metal when the temperature T is less than $1{\cdot}157\times 10^4\, V_0$,

$$(\chi_A)_e = 32{\cdot}1\,(q/V_0)\left\{1-6{\cdot}11\times 10^{-9}\left(\frac{T}{V_0}\right)^2\right\}\times 10^{-6},$$

where q is the number of quasi-free electrons per atom and V_0 is the width of the energy band, or the maximum electron energy in the completely degenerate state, expressed in equivalent volts. Neglecting the second term in the above expression and substituting $(\chi_A)_e = 3{\cdot}20\times 10^{-6}\times 52{\cdot}01$, we find $V_0/q = 0{\cdot}2$ volt, while the value estimated by Sommerfeld and Bethe using other data is 0·34 volt. These values are too low, so that it may reasonably be assumed that several electron-energy bands overlap and thus make the effective number of energy states greater. For example if it is assumed that five energy bands, corresponding to the five energy states of th *d* electrons overlap, then the calculated values of V_0 become five times as great a those above. Or we may say that the density of states at the top of the Ferm distribution is much larger than it would be for free electrons, or that positiv interchange interaction effects occur, or that both these factors are effective.

It is of interest to compare the temperature-variation required by the abov theory with that found in our experiments. Thus we find $\chi_A = 3{\cdot}198 \times 10^{-6} \times 52{\cdot}$ at 293° K. and $3{\cdot}098 \times 10^{-6} \times 52{\cdot}0$ at 619° K., when no correction is applied fo expansion but correction is applied for diamagnetism of the core. If we take the coefficients of linear expansion of chromium and pyrex to be 9·7 and $3{\cdot}0 \times 10^{-6}$ pe degree respectively, then the value of the atomic susceptibility at the latter temperature when corrected for expansion is $3{\cdot}119 \times 10^{-6} \times 52{\cdot}0$. Hence

$$\Delta(\chi_A)/\Delta T = 0{\cdot}0126 \times 10^{-6}.$$

The theoretical value is $-32{\cdot}1\,(q/V_0^3)\;6{\cdot}11 \times 10^{-9} \times 2T \times 10^{-6}$, whence taking $T = 450$ approximately, $q = 6$ and $V_0 = 1{\cdot}2$ volts, we get the value $0{\cdot}000613 \times 10^{-6}$. The experimental value is therefore some twenty times as great as the theoretical value, on the assumption that $q = 6$. Lower values of q would give an approximate agreement, and, indeed, are possible, since it is only the electrons in unfilled (or partial) bands which contribute to the susceptibility. Moreover, the equation used above is based on the assumption that the energy-distribution of states of the q electrons in the unfilled band is of the same type as that for free electrons, and this may not be an adequate basis of discussion.

§7. ACKNOWLEDGMENTS

The magnetic measurements were made with an electromagnet constructed with a grant kindly made to one of us by the Government Grants Committee of the Royal Society. We desire to extend our cordial thanks to Mr H. Terrey for advice on the chemistry of chromium and to Prof. E. N. da C. Andrade for the many facilities afforded us.

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THE MAGNETIC PROPERTIES OF AMALGAMS

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BSTRACT. The magnetic susceptibilities of a series of amalgams of known concentraons of bismuth, chromium, copper and manganese with mercury have been studied at room mperature, the Gouy method of measurement being employed in all cases. A study of he drop-weight method of measuring susceptibilities showed it to be quite unreliable for easurements with amalgams. In dilute amalgams manganese was found to possess an pparent atomic susceptibility of $+13{,}7000\times10^{-6}$, bismuth $+133\times10^{-6}$, chromium 23×10^{-6} and copper about $-7{\cdot}3\times10^{-6}$ e.m.u. All metals so far studied which are diaagnetic in the solid state are paramagnetic in dilute amalgams, with the possible exception f copper.

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§ 1. INTRODUCTION

IT is somewhat remarkable that in spite of its importance to the theory of the metallic state and to the theory of magnetism in particular, no systematic survey of the magnetic properties of the alloys or amalgams of mercury with other lements has been made. It is still more remarkable, however, that the generally ccepted value for the susceptibility of the element mercury itself is now known to e seriously in error. The experiments described below were undertaken to supply ome information concerning the magnetic properties of those amalgams which were f more immediate interest to us in connection with other work, but the opportunity vas taken to redetermine the susceptibility of pure mercury and to examine certain pecial features of amalgams.

The value given for the mass susceptibility of pure mercury in the *International ritical Tables* (1926) is $-0{\cdot}19\times10^{-6}$ e.m.u. per gram, a value derived from the vork of Honda (1) and of Owen (2), who both used the Curie translation method of neasurement. The values of susceptibility in different fields show quite clearly that n Owen's experiments the mercury contained some form of ferromagnetic impurity, ut Honda states that iron could not be detected in the specimen of Kahlbaum nercury used by him, and the observed susceptibility was independent of the ield-strength. Honda's value was $-0{\cdot}193\times10^{-6}$ e.m.u. per gram. Owen elimiated the effects of the ferromagnetic impurity by means of the relation*

$$\chi_\infty=\chi_H-\frac{\sigma}{H} \qquad \ldots\ldots(1),$$

vhere χ_∞ is the true value of the susceptibility in a very large field, χ_H the experi- χ_∞, χ_H

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* This equation is correct for measurements by the Curie method. Vogt has pointed out that σ ust be replaced by 2σ when measurements are made by the Gouy method.

mental value obtained when a field H is employed and σ is the saturation magnetization per gram of the ferromagnetic impurity present. Owen states that his Kahlbaum specimen of mercury contained less than 0·0001 per cent of iron, and his measurements indicate that σ was of the order of $0{\cdot}06 \times 10^{-3}$ c.g.s. unit per gram; the valu for χ_∞ is given as $-0{\cdot}184 \times 10^{-6}$ at 20° C.

It is surprising that these values have been accepted for so long without comment in fact, until the susceptibility of liquid and solid mercury was redetermined b Vogt(3) in the course of his work on the magnetic properties of single crystals o pure mercury, the value then obtained being $-0{\cdot}168 \times 10^{-6}$ at 20° C. Vogt obtaine this value by comparison of the susceptibility of mercury with that of water; an it is confirmed by our experiments. It is therefore unfortunate that his wor appears to be unknown to the compilers of physical tables more recently published Turning now to the work on magnetic properties of amalgams, only two publishe papers are known to us. The first, by Gnesotto and Binghinotto(4), quoted in th *International Critical Tables*, deals with amalgams of bismuth and mercury. Th second is by Davies and Keeping(5), who worked with dilute amalgams of gold, tin indium, and gallium with mercury. In addition, we find a statement by Bhatnaga and Mathur(6) that dilute liquid amalgams of copper are merely mechanical mixture of the two metals in which the value of the magnetic susceptibility varies from tha of pure mercury to that of pure copper. However, all these workers were satisfied that the correct value of the susceptibility of pure mercury was $-0{\cdot}190 \times 10^{-6}$ Davies and Keeping checked this value by comparison with pure water and stat that they obtained the value $-0{\cdot}189 \times 10^{-6}$. Bhatnagar and Mathur, it is true, mad no direct statement concerning the susceptibility of mercury, but the value recorded in their tables is $-0{\cdot}19 \times 10^{-6}$. We therefore conclude that the results so far obtained with amalgams are qualitative only, although some of them are certainly of interest It is felt that the main reason for the errors found in the above measurements lies i the comparison methods used. In general it was not possible to make the series o measurements required for the application of the Owen-Honda correction, equatio (1), and thus to see what part ferromagnetic impurities played.

§ 2. METHOD

In view of the facts outlined above it was considered essential to employ a direc or absolute method for measuring the susceptibility in the experiments now described. The apparatus is shown diagrammatically in figure 1. It consisted of th uniform pyrex glass tubes A and B which were suspended as shown from one arm of a sensitive chemical balance. The upper tube contained the mercury or amalgam under investigation, while the lower was evacuated. As both were cut from th same piece of pyrex tubing they were practically of the same cross section, and th lower tube acted as a compensator for the magnetic effects of the air displaced by th glass and liquid. They were connected together by a short piece of fine copper wire and their adjacent ends were situated in the uniform magnetic field between th pole pieces NS of an electro-magnet of convenient design(7). Let us suppose tha magnetic pull on the apparatus for a field H is δm_0 when A is evacuated, $\delta m_a + \delta m_0$ en A is filled with air, and $\delta m_0 + \delta m_{Hg}$ when A is filled with mercury. Then the ual Gouy formula may be used for the magnetic force on column of mercury surrounded by air, viz.

$$(+\delta m_{Hg} - \delta m_a) . g = \tfrac{1}{2} (k_{Hg} - k_a) . \alpha . H^2 \quad \ldots\ldots(2),$$

ere α is the area of cross section of the mercury in the be and k_{Hg}, k_a are the susceptibilities of mercury and air spectively. In like manner, when the tube A contains algam with susceptibility k_{am}, we have

$$(\delta m_{am} - \delta m_a) . g = \tfrac{1}{2} (k_{am} - k_a) . \alpha . H^2 \quad \ldots\ldots(3),$$

ence

$$k_{am} = k_{Hg} - \left(\frac{\delta m_{Hg} - \delta m_{am}}{\alpha . H^2} \right) . 2g \quad \ldots\ldots(4).$$

the last equation k_{Hg} and in general k_{am} are negative. It ill be noted that, provided the value of k_{Hg} is accurately own, the susceptibility of an amalgam may speedily be easured by finding the difference between the magnetic rces on pure mercury and the amalgam for a chosen value H. The field H was measured with a Grassot fluxmeter hich was calibrated by measuring the magnetic pull on solution of nickel chloride of known susceptibility.

δm_0, δm_a

δm_{Hg}

g

α

k_{Hg}, k_a

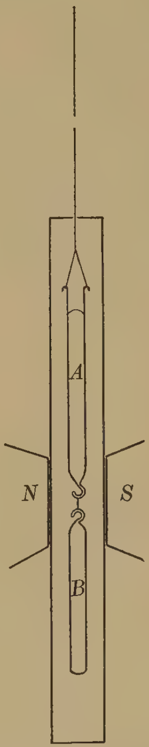

Figure 1. Arrangement for measurement of magnetic susceptibilities of amalgams by the Gouy method.

§ 3. PREPARATION OF MATERIALS

The mercury used in the present experiments was prepared as follows. After prolonged bubbling with air the ercury was washed in dilute nitric acid, in a dilute solution potash and in water, and was finally dried. It was then istilled in a quartz vacuum still, so that all heavy metal npurities were removed. To ensure the removal of lighter nd more volatile metals the mercury was redistilled in a form of apparatus like that escribed by Hulett(8) in a stream of air at a pressure of about 25 mm. of mercury. he amalgams were usually prepared by electrolysis, although in some cases they ere prepared by mechanical mixing. The purest materials available were used, and agnetic tests were always made for the presence of ferromagnetic impurity. etails of the individual preparations are given below.

§ 4. EXPERIMENTAL RESULTS

Mercury. The volume susceptibility of mercury at 18° C. was first found. The alues of the $(+\delta m_{Hg} - \delta m_a)/H^2$ are plotted against the corresponding values of $/H$ in figure 2, from which the value of $(k_{Hg} - k_a)$ was found to be $2{\cdot}303 \times 10^{-6}$, hence, taking the volume susceptibility of air as $0{\cdot}031 \times 10^{-6}$ and the value 13·565 or the specific gravity of mercury at 18° C., the value of the mass susceptibility of ercury is $-0{\cdot}1675 \times 10^{-6}$ e.m.u. per gram, which is in excellent agreement with the value found by Vogt. The results shown in figure 2 prove conclusively that ferromagnetic impurities were not present in this mercury. The value $0{\cdot}168\times10^{-6}$ per gram or $2{\cdot}284\times10^{-6}$ per cm³ is taken as correct throughout the following work.

Manganese amalgam. As manganese amalgams were of special interest to one of us, experiments were first made with them. The amalgams were prepared by electrolysis of a solution of manganese chloride, a cup of mercury forming the cathode and a platinum plate the anode. The latter was surrounded by a porous pot filled with a solution of manganese sulphate. The amalgam was quickly washed in distilled water and poured into the tube *A* which was then placed in a desiccator. The latter was evacuated through drying-tubes, and by violent shaking the amalgam was freed from water and air bubbles. On account of the small percentages of manganese used in these experiments, and because some manganese is deposited on the anode as MnO_2, the amount of metal present in a given amalgam was always determined directly by colorimeter measurements. A small known mass of the amalgam was dissolved in nitric acid, and a little silver nitrate was added. Ammonium persulphate was added to the liquid and on boiling the usual permanganate colour resulted. The liquid was made up to a known volume on cooling and its colour compared with that of a standard solution of known manganese content, using a Bausch and Lomb colorimeter. The individual concentration measurements are no highly accurate, because of the well-known limitations of such measurements.

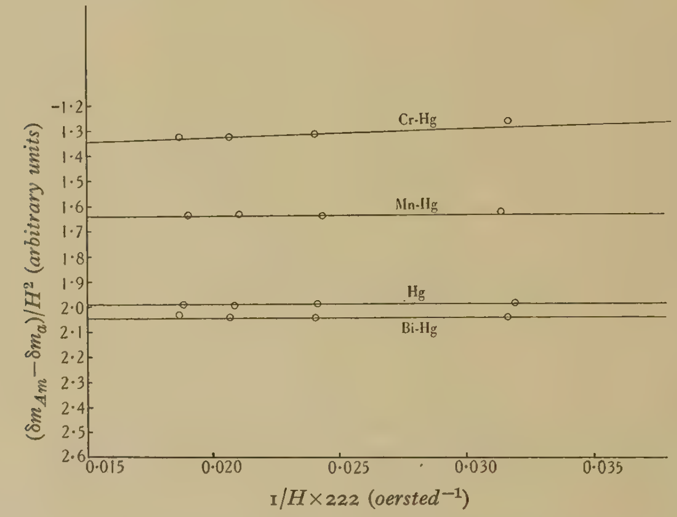

Figure 2. Graphs of observed susceptibility, plotted against $1/H$ to give the correction, if any, for ferromagnetic impurity.

The susceptibility measurements are shown in figure 3 where the volume susceptibility is plotted against percentage concentration by weight of manganese in the amalgam. The mass susceptibilities may be obtained by dividing the values in ure 3 by the density of mercury, since the density of the amalgam containing 257 per cent of manganese was 13·547 g./cm.^{3} Two tangents have been drawn to is curve, and the slope of that passing through the value for pure mercury gives e variation of susceptibility with concentration of amalgams of very low man-nese content. The slope in question is considerably greater than that of the ngent drawn to the curve at higher concentrations. This is an interesting feature d is in accord with other experiments on manganese.

If we consider that m g. of a metal of mass susceptibility χ_M are amalgamated ith $(100-m)$ g. of mercury, giving an amalgam of volume susceptibility k_{am} and nsity ρ, we may write

χ_M
k_{am}
ρ

$$100\ k_{am}/\rho = m.\chi_M + (100-m)\ \chi_{Hg}.$$

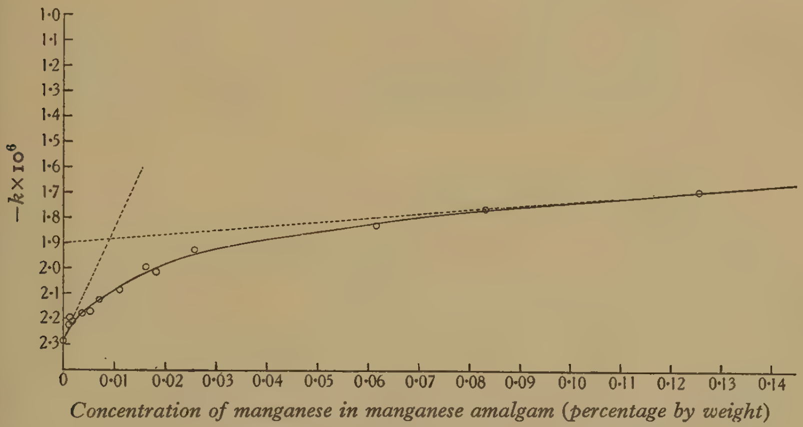

Figure 3. Magnetic susceptibility of manganese amalgams.

n differentiating and rearranging the terms, we have

$$\chi_M = \frac{100}{\rho}\frac{dk_{am}}{dm} + \chi_{Hg},$$

rom which the atomic susceptibility of the metal may readily be found. In this alculation it is assumed that the metal does not combine with the mercury to form new compound. If, however, one atom of the metal combines with n atoms of ercury to form a chemical compound whose magnetic susceptibility is χ_C, then he above equation becomes

n
χ_C

$$\chi_C = \frac{100}{\rho}\ \frac{1}{1+n.M_{Hg}/M}\ \frac{dk_{am}}{dm} + \chi_{Hg},$$

here M_{Hg} is the atomic weight of mercury and M that of the metal; χ_C is therefore ss than χ_M, and this should be remembered in discussing the properties of malgams of high concentration.

M_{Hg}

From the slope of the first tangent we find that the molar susceptibility of man-anese in very dilute solution in mercury is about $13{,}700\times 10^{-6}$; in view of uncer-ainty in the concentration measurements the value is not regarded as very accurate.

It is, however, interesting to note that it agrees with the results obtained by othe workers for dilute solutions of manganese in other metals, which are contained in table 1.

Table 1

Alloy of manganese in:	Atomic susceptibility of manganese × 10^6	Authors
Aluminium	+ 1,600	Auer(9)
Copper	13,400	Néel(10)
Silver	11,300	Néel(10)
Copper	13,400	Valentiner and Becker(11)
Mercury	13,700	Bates and Tai
Manganese (pure)	648	Bates and Reddi Pantulu(1

The value for the differential atomic susceptibility of manganese in more concentrated amalgams obtained from the slope of the second tangent is $+674 \times 10^{-6}$. The amalgams were tested for ferromagnetic impurity, and a set of results is shown in figure 2.

§ 5. DROP-WEIGHT MEASUREMENTS

It is convenient here briefly to describe some experiments which we made on these amalgams by the drop-weight method, which was originally devised by Athenasiadis(13) and has been shown by Abonnenc(14) to give a satisfactory method of comparing the susceptibilities of solutions and liquids which do not differ too markedly in their physical properties. The principle is as follows. A liquid is allowed to drop slowly from a jet in a magnetic field H whose gradient dH/dx in a downward direction over the region occupied by a forming drop is considerable.

m, m' If the mass of each drop in the absence of a magnetic field is m, then the mass m' in the presence of the field will depend upon the magnitude of the magnetic force which will either pull the drop downwards or assist in its support. It is easy to show that, provided the surface tension of the liquid remains constant, the relation between m and m' is given by

$$\chi_l - \frac{k_a}{\rho} = \left(\frac{m-m'}{m'}\right) g \Big/ H.\frac{dH}{dx} \qquad \text{......(5),}$$

χ_l where χ_l is the mass susceptibility of the liquid. It was felt that as this method automatically avoided the necessity for density-measurements, since the term $k_a/$ is very small, and as it appeared that very small quantities of the material would be required, it might be used with advantage for determinations made with amalgams of manganese where large changes of χ_l were expected, and actually many such measurements were made before the Gouy method was employed. In our view, this work showed that the method is of very limited application, that only very dilute amalgams can be used in it, and that it is definitely unreliable in the case of manganese. The apparatus used is shown diagrammatically in figure 4, where the jet J was placed between the shaped pole pieces P of an electromagnet. The mercury or the amalgam was placed in the glass apparatus A shown in the lower portion of the figure, and by pressing the valve bulb B the liquid was forced into the tube J

hich was placed in position around the jet J. The length LL of capillary tubing, bout 0·75 mm. in bore, was constricted at C, in the manner adopted in apparatus esigned by Iredale(15) for the determination of the surface tension of mercury. The orizontal portions of LL were in the same horizontal plane as the orifice of J, and e end of the tubing remote from the field was bent as shown so as to be covered by e mercury in the reservoir R, which could be raised by the movable stand S. The nd E lay below the orifice J, and when it was connected by rubber tubing to a ater pump, the liquid under investigation could be sucked into LL with ease. The vel of the mercury in R was previously adjusted to maintain the liquid in position. t will be noted that measurements were confined to the amount of liquid contained n LL, whose total length was about 80 cm. J' was then removed.

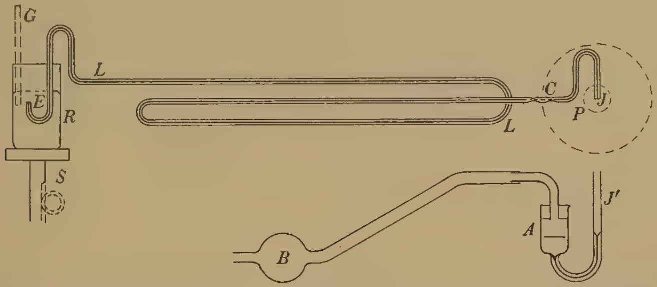

Figure 4. Apparatus for use in determination of magnetic susceptibility of amalgams by drop-weight method.

The following procedure was adopted. The liquid was forced out of J by lowering he glass plate G into the reservoir to give a higher initial head of mercury, and when he drop was nearly formed G was removed, and the final stages of the drop-formaion were slowly assisted by raising the table S. Three drops were allowed to fall nto a collecting vessel X when the field was not excited; then the field was switched n and three drops were collected in a vessel Y in the cases when pure mercury was sed. When an amalgam was used a drop was also allowed to fall into a vessel T etween the foregoing collections. Several such series of drops were collected and weighed and the corresponding values of m and m' were found. The drops in the vessel T were used in concentration-measurements as described above. To prevent xidation of the amalgams and consequent change in weight, the vessels X and Y ontained a little paraffin oil.

The constrictions C were very necessary to reduce the rate of drop-formation, ut unfortunately only relatively dilute amalgams could be passed through them even when the constrictions were so wide that the rate of the drop-formation was oo high. Yet the values of the ratio $r=(m-m')/m$ for pure mercury taken on successive days with the same field current were surprisingly constant, as is shown n table 2.

Table 2

$m-m'$	0·2240	0·2235	0·2253	0·2236	0·2235	0·2252	0·2245 g.
r	0·06645	0·06630	0·06676	0·06628	0·06647	0·06718	0·06697

Such differences as are observed could easily be due to field-changes. If we first
pure mercury in the apparatus, we have

$$\chi_{Hg} - \frac{k_a}{\rho} = \left(\frac{m-m'}{m'}\right)_{Hg} .g/H.\frac{dH}{dx} = (r)_{Hg}.g/H.\frac{dH}{dx},$$

and on using an amalgam we have in like manner

$$\left(\chi_{am} - \frac{k_a}{\rho}\right) = \left(\frac{m_1 - m_1'}{m_1}\right)_{am} .g/H.\frac{dH}{dx} = (r)_{am}.g/H.\frac{dH}{dx},$$

so that

$$\left(\chi_{am} - \frac{k}{\rho}\right) = \left(\chi_{Hg} - \frac{ka}{\rho}\right) (r)_{am}/(r)_{Hg} \qquad ......(6).$$

The results of measurements made by this method are shown in figure 5, wh
the pronounced peak is very striking. We are confident that this peak prope
represents the results obtained by the drop method. The value for the susceptibilit
of amalgams whose concentrations lie to the right of the peak are definitely m

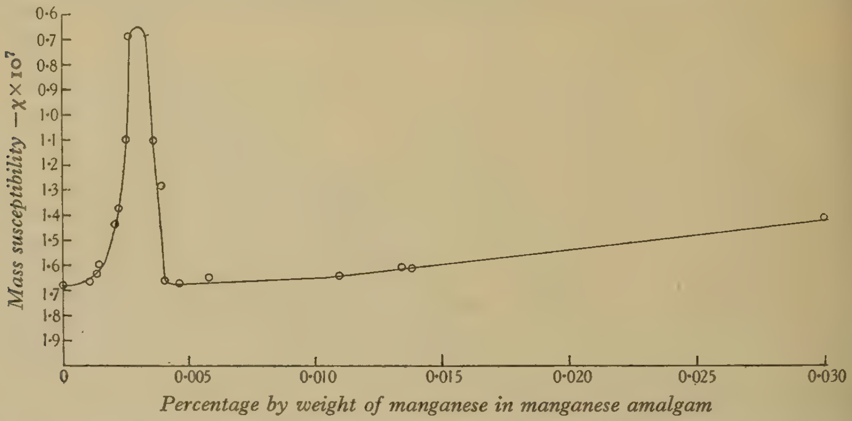

Figure 5. Magnetic susceptibility of manganese amalgams obtained by the drop-weight meth
The pronounced peak is regarded as incorrect and as showing that the drop-weight method
unreliable for amalgams.

lower than those obtained by the Gouy method, although at much greater conce
trations than those shown in the figure the agreement between the results was mo
satisfactory; but it was only by good fortune that isolated values at high concentr
tions could be obtained by the drop-weight method.

The presence of the peak caused much concern until we found that Royce a
Kahlenberg(16), in their study of the electrode-potentials of manganese, recorded t
manganese formed a saturated but very dilute solution in mercury containing on
0·0032 per cent of manganese, throughout which solid Mn_2Hg_5 was dispersed. Th
is precisely the concentration at which the peak occurs in figure 5. The success of th
drop-weight method depends upon the constancy of the surface tension of the flu
both in and out of the magnetic field. The curve in figure 3 indicates that the dilu
solution is more paramagnetic than the solid Mn_2Hg_5, so that on the application
the field the lumps of the latter should tend to leave the upper portions of the dro

d the surface tension would thereby be changed; it is considered that such anges would be at their maximum when the saturation limit is reached and ould decrease as the amount of Mn_2Hg_5 increased. This, of course, does not mean at we have discovered that a magnetic field directly affects the surface tension of fluid, for then it would also affect adsorption processes, and the circumstances in e case of these amalgams clearly do not approximate to those of homogeneous lutions. The phenomenon is interesting but leads to no definite theoretical eductions. It may be noted in passing that to explain the peak on the above lines e apparent surface tension of the drop must be increased by the presence of the eld.

Bismuth. Bismuth amalgams were prepared by the complete denudation of a lution containing a known quantity of pure bismuth nitrate and a trace of merurous nitrate, a known quantity of mercury being used as cathode and a platinum il as anode, with a fairly high current. The weaker amalgams were quite fluid but the more concentrated ones showed a tendency to solidify. The percentages of bismuth were calculated on the assumption that all the bismuth in the electrolyte solution was sent into the mercury and the denuded solution was always tested with H_2S for the presence of the metal before electrolysis was discontinued. The amalgams were placed in the tube *A* and evacuated as described above. Bismuth amalgams are relatively easy to handle as they oxidize but slowly, and the same mercury can be used for several electrolytic depositions.

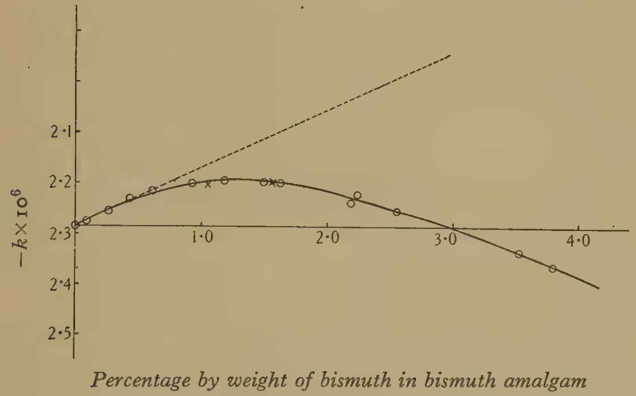

Figure 6. Magnetic susceptibility of bismuth amalgams.

⊙ Amalgam obtained by electrolysis.
× Amalgam obtained by mechanical mixture.

The curve showing volume susceptibility against concentration is drawn in figure 6. The initial increase in susceptibility was rather unexpected, but its correctness was checked by further measurements on amalgams made by mechanically mixing pure metallic bismuth with mercury, the two sets of results being in very good agreement. The points marked as crosses on the curve were obtained with mechanically mixed amalgams. The tangent at the origin of the curve shows that bismuth enters into dilute solution in mercury as if it possessed an atomic susceptibility of $+133 \times 10^{-6}$ instead of -293×10^{-6}. The final slope of the curve corresponds to an atomic susceptibility of about -182×10^{-6}, although, owing to the tendency of the amalgam to solidify, this value is not considered to be of high accuracy; these figures are calculated on the assumption that the mass susceptibility is equal to the volume susceptibility divided by 13·51, the specific gravity given for a 1-per-cent amalgam of bismuth and mercury in the new edition of Landolt-Bernstein's tables.

At first sight it might appear that the peculiar shape of the curve in figure 6 is due to the presence of impurities in the bismuth, but this is not likely to be the case, for the amount of impurity should be directly proportional to the amount of bismuth introduced in the electrolysis preparations, and hence if bismuth really gives a linear relation it should persist. Moreover, we had good agreement with the check determinations carried out upon amalgams made with solid bismuth, and the bismuth line in figure 2 shows that no ferromagnetic impurity was present. Indeed, the appearance and the behaviour of the amalgams were most satisfactory, and as the mercury was changed frequently in the course of the determinations, and measurements were made with various concentrations in different portions of the curve at intervals some days apart, the curve must be regarded as well established. In addition, some samples were allowed to stand in the tube *A* for as long as forty hours without any change in susceptibility being observed, so that no change due to lapse of time can be involved. As has already been mentioned, the graph shown in the *International Critical Tables* is a straight line joining the values taken for the susceptibilities of pure bismuth and pure mercury, but as the latter value is in error by some 13 per cent we must disregard this work. Moreover, the melting-point diagram(17) for amalgams of bismuth and mercury shows a distinct phase change at a concentration of about 5 per cent of bismuth, which is outside the range of our experiments, and a pronounced change in susceptibility would certainly be expected there as well.

If, however, the large diamagnetism of bismuth can be attributed to the existence of large electron orbits which enclose many atoms in the solid state, as has been suggested by Ehrenfest, then a more ready explanation of part of the initial changes shown in figure 6 arises. For these orbits must be expected to disappear when bismuth enters the liquid state and thus the sudden decrease in diamagnetism from -213 to $-16{\cdot}7 \times 10^{-6}$ per gram-atom of bismuth on melting would be explained. In like manner, the large electron orbits would be expected to disappear totally in very dilute amalgams, but some traces of them might appear as the concentration of bismuth and the noticeable tendency to solidification increased. However, the experiments show that bismuth in low concentration behaves as a paramagnetic, and the disappearance of the large orbits is not sufficient to account for all the initial changes observed. A different explanation of the great susceptibility of solid bismuth has recently been given by Jones(18), who examined the Brillouin zones of energies occupied by loosely bound electrons in alloys with a γ structure, and showed that the lowest group of energy levels is filled by a number of such electrons in accordance with the Hume-Rothery rule. These electrons account for the large magnetic susceptibility of these alloys, and Jones deduces by analogy that the stence of a Brillouin zone in solid bismuth, containing just five electrons per m, accounts for the high value of the susceptibility, and its disappearance may ount for the paramagnetic behaviour of bismuth in the amalgam. It would be eresting to carry out experiments to determine the {susceptibility, concentration} ve at different temperatures, particularly for dilute amalgams, and this we prose to do in the near future.

Chromium. The properties of chromium amalgams were of interest to one of us cause they were used in the preparation of specimens of metallic chromium whose gnetic properties were recently investigated. These amalgams present rather mplicated problems. In the first place, chromium amalgams break down rapidly the presence of water, so that they had to be washed as quickly as possible in solute alcohol before being placed in tube *A*. In this process some decomposition the more concentrated amalgams was bound to occur, and there was evidence that e product of the decomposition, a black powder which floated on the mercury rface, was slightly ferromagnetic. In the second place it was most inadvisable to e a particular sample of mercury for more than one chromium electrolysis; the nalgams decomposed on standing in contact with air, although we reduced this ect to a minimum by placing a little oil on the surface in the tube *A*.

The amalgams were prepared by complete electrolysis of solutions of $r_2(\mathrm{SO}_4)_3 \cdot 7\mathrm{H}_2\mathrm{O}$, supplied by Hopkins and Williams, to which a little free sulphuric id was added; the disappearance of colour indicated that electrolysis was complete. heavy current had to be passed for some hours to obtain the largest concentrations ed in these experiments, the vessel containing the electrolyte being cooled by an -blower; it seems practically impossible to obtain higher concentrations by the ctrolysis method. With chromium salts there is always a danger of iron being esent; actually our specimens seem to have been fairly free from this impurity, as as shown by experiments on the chromium prepared by distilling off the mercury. he chromium line of figure 1 shows that some ferromagnetic impurity was present, d it was attributed to the products of decomposition referred to above.

The results are shown in figure 7, and it is seen that the curve consists of two rts, although this division is attributed to partial decomposition of the amalgam. he results were obtained with amalgams whose appearance was very satisfactory, r when decomposition was observed to be present the observed susceptibilities ere erratic, particularly in the transition region. The chromium line of figure 1 fers to the point *A* on the curve in figure 7, and it is found that even when full eight is given to the point corresponding to the lowest field in applying the wen-Honda correction for ferromagnetism, the calculated value of the susceptility is changed only slightly, to *B* in figure 7.

The tangent to the curve at the lowest concentrations which showed no traces of rromagnetism shows that chromium in dilute solution behaves as if it possessed an omic susceptibility of $+23 \times 10^{-6}$ units, as compared with the value 160×10^{-6} cently found by Bates and Baqi for the solid metal.

Copper. The following experiments were carried out on copper because we wished to satisfy ourselves that the statement that amalgams of copper and mercury are merely mechanical mixtures was correct. The greatest difficulty was found in obtaining pure copper, and all the copper amalgams we were able to make must have contained iron. We first electrolysed solutions of Analar copper sulphate crystals certified to contain less than 0·015 per cent of iron, but all the amalgams of concentration greater than 2 per cent of copper showed very pronounced ferromagnetism.

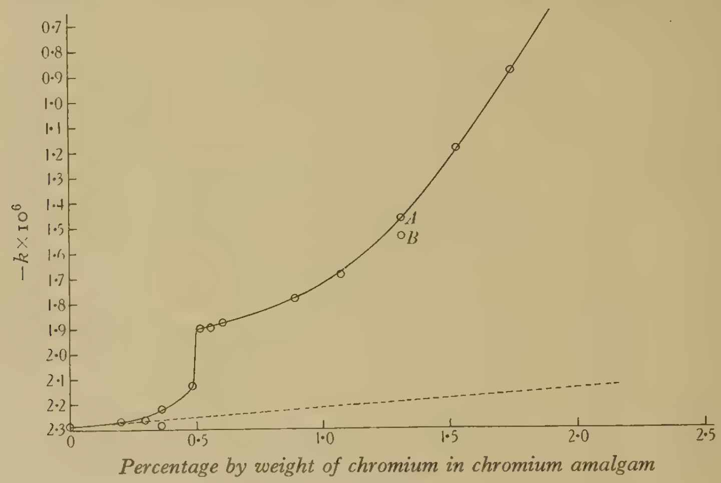

Figure 7. Magnetic susceptibility of chromium amalgams.

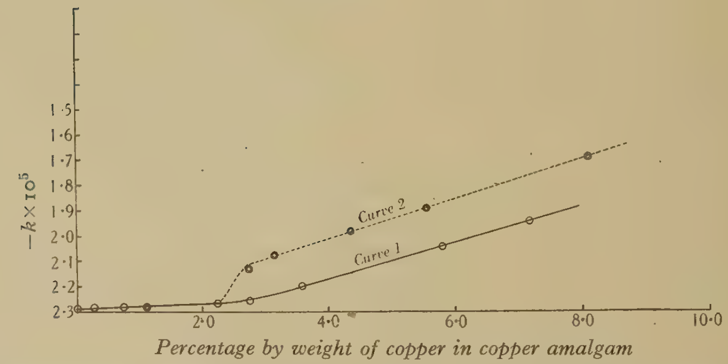

Figure 8. Magnetic susceptibility of copper amalgams. Curve 1, amalgam containing least ferr magnetic impurity. Curve 2, amalgam obtained from electrolysis of solution of electrolyt copper dissolved in sulphuric acid.

We next made solutions of pure electrolytic copper dissolved in nitric acid, but thes too, were unsatisfactory, and our most satisfactory results from the point of vie of ferromagnetic impurity were obtained by dissolving copper, provided by Johnso and Mathey for analytical purposes, in nitric acid.

In curve 1 of figure 8 are shown the values of the volume susceptibility of coppe amalgams obtained with the last kind of solution. The curve showing mass suscepti bility against concentration is very similar because the density of an amalga ntaining 8 per cent of copper was found to be 13·494 g./cm.^{3} Hence it is clear that, th our amalgams at any rate, there is no sign of the linear relation which mere echanical mixtures of copper and mercury would require, except in the case of ry dilute amalgams where copper enters into solution with a susceptibility of about 0·12 × 10^{-6} e.m.u. per gram. The magnitude of the ferromagnetic corrections may gauged from the Owen-Honda lines for the more concentrated amalgams shown figure 9.

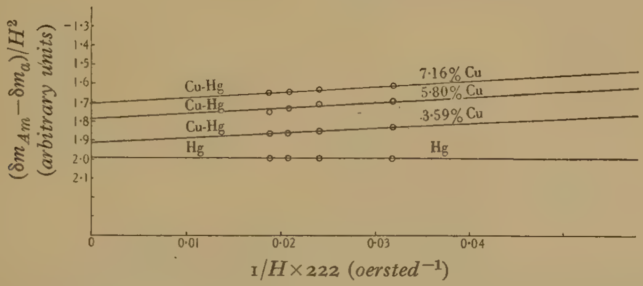

Figure 9. Copper amalgams. Graphs of observed susceptibility plotted against $1/H$ to give the correction for ferromagnetic impurity.

It is of interest to consider the effects of more pronounced ferromagnetic impurity found in the case of the second kind of solution, that of pure electrolytic opper, which has been described above. Some results were obtained by direct omparison of the magnetic forces acting on the several amalgams with that on ercury, the Gouy method, with a maximum field of 11,800 oersteds, being used. he values for more concentrated amalgams lie on a straight line, curve II, which lmost passes through the point corresponding to pure mercury, but again the values or the weak amalgams lie on the initial portion of curve I. It appears that the erromagnetic nature of iron in the mercury is only effective when a certain concentraion is exceeded. This is a point of some interest to us and we propose to investigate he magnetic properties of iron, nickel, and cobalt in mercury in a separate research. When ferromagnetism is present there is always an ill-defined region between the nitial and final portions of the curve II where the transition from one branch to the ther occurs. This seems to be a characteristic of ferromagnetic impurity, and we ave already mentioned its occurrence in the experiments on the chromium malgams.

§ 6. DISCUSSION OF EXPERIMENTAL RESULTS

In table 3 are collected the values for the atomic susceptibilities of metals in ilute solution in mercury. The values for gallium, gold, indium and tin have been btained from the results of Davies and Keeping$^{(5)}$ by use of the equation

$$(\chi_M)_A = M.\left\{100.\left(\frac{d\chi_{Am}}{dm}\right) - 0{\cdot}190\right\}\frac{168}{190}.$$

The factor 168/190 is introduced because these workers took the mass susceptibility of mercury to be 0·190 × 10^{-6} instead of 0·168 × 10^{-6}, but its introduction does n t materially affect the conclusions to be drawn from the table.

Table 3

Metal	$(\chi_M)_A \times 10^{+6}$	
	In the solid state	In amalgam
Mn	+648	+13,700
Cr	+160	+ 23
*Sn	+ 3	− 10
Cu	− 5·4	− 7·3 ?
*In	− 16·3	+ 218
*Ga	− 16·7	+ 133
*Au	− 29·6	+ 194
Bi	−293	+ 133

* Results obtained from Davies and Keeping's paper.

The striking fact which emerges is that each of the diamagnetic metals, with th possible exception of copper, behaves as a paramagnetic in dilute solution in mercur It is clear that valuable information may be obtained by studying the temperatur variation of this paramagnetism, and this we propose to do. The data for metal which are paramagnetic in the solid state are too scanty to permit of deductions, an we propose to study other amalgams at room temperature. The high values fo manganese and bismuth are in accord with the fact that MnBi is ferromagnetic we also propose to examine the amalgam of manganese plus bismuth.

The changes in magnetic susceptibility on solution, shown in table 3, are sup ported by the work of Skaupy(19) on the electrical conductivities of amalgams con taining small quantities of dissolved metal. He refers to the well-known fact tha the conductivities of such amalgams containing the metals lead, zinc, cadmium etc are greater than that of pure mercury, whereas the conductivities of solid solution or of mixed crystals are always less than that of the solvent metal. These increase of conductivity may be attributed either to an increase in the number n of free elec trons or to a decrease in the viscosity η, and Skaupy deduces that $n = A . \eta . \sigma_{am}$, wher σ_{am} is the conductivity of the amalgam and A is a constant. An increase in n would clearly be found if the dissolved atoms lost electrons on solution, when a form o chemical equilibrium would exist between the dissolved metal and the mercury since both contain a common constituent, the electron. Such equilibrium would, o course, be modified by change in temperature, and for the interpretation of the magnetic results for a series of temperatures it would apparently be necessary t obtain the relevant conductivity data.

§7. ACKNOWLEDGMENTS

The magnetic measurements were in part made with an electro-magnet constructed with a grant to one of us from the Government Grants Committee of the Royal Society. We are indebted to Mr H. Terrey for much information on the chemistry of amalgams, to Prof. C. A. Lovatt-Evans for the loan of a colorimeter, and to Prof. E. N. da C. Andrade for the facilities afforded us.

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REVIEWS

The Quantum Theory of Radiation, by W. HEITLER. Pp. xi + 252. (Clarendon Press, Oxford: Humphrey Milford, 1936.) 17*s*. 6*d*. net.

This treatise gives an admirably clear and comprehensive account of the numerous physical applications of the quantum theory of radiation. Researches into the quantum theory may be broadly divided into two groups—the practical and the speculative. Both groups of researches start from the formulation of the quantum theory due to Dirac and Heisenberg. The object of the practical investigations is the direct application of this form of the theory to problems of experimental physics. The speculative investigations aim at a more complete and perfect formulation of the theory in which the number of axioms shall be reduced to a minimum and their effective range of application increased to a maximum. It is no derogation from the universally recognized genius of the authors of the contemporary form of the quantum theory to point out that the theory of the interaction of electric charges has no very satisfactory basis and that it is hardly wide enough for the thorough treatment of relativistic questions. In fact the theory of interaction is the outstanding problem of speculative quantum theory.

The present work is devoted entirely to the practical researches, although, of course, it indicates all the points at which the accepted theory is incomplete. It opens with a very welcome summary of the classical theory of radiation, which is treated so as to provide an introduction to the methods and technique adopted in the quantum theory of radiation. The author then discusses the quantum theory of the field *in vacuo* with especial reference to the uncertainty relations connecting the field strengths. The third and main section of the book deals with the interaction of matter and radiation, including processes of the first order such as emission and absorption, processes of the second order such as dispersion and the Raman effect, and processes of the third order such as the continuous X-ray emission. The two concluding sections discuss radiation processes connected with positive electrons and the penetrating power of high energy radiation.

This monograph presents the first systematic report on these important topics and it is indispensable not only for the theorist engaged in practical or speculative research, but also for the experimentalist who desires to know how far observations of interaction processes can be interpreted by the quantum theory. The book is beautifully produced and printed and there is a good index.

G. T.

Werkstoffkunde der Hochvacuumtechnik, by W. ESPE and M. KNOLL. Pp. viii + 383. (Berlin: Julius Springer, 1935.) RM. 36 (58*s*. 6*d*.).

The title of this book, which may be roughly rendered "Materials used in the High-Vacuum Industry", does not, perhaps, indicate at first sight how extremely useful it may be to the physicist engaged in practically any experimental research. The authors, who are closely connected with the great Siemens-Konzern, and thus possess special facilities and advantages for compiling a work of this kind, have assembled a body of exact information on the properties of metals, glasses and other substances, such as phosphors, used in what may be called the electrical tube industry, and on the preparation and working of those materials. A great deal of the information has not hitherto been accessible, at any rate to those outside industry, without the greatest trouble: most of it has been published, it is true, but generally in such places as the *Veröffentlichungen* of the Siemens-Konzern, the Osram-Konzern and other corporations; in technical journals which are found in very ew English libraries; or in patent specifications. The ordinary standard tables do not eadily, if at all, yield the figures here given, and the standard books on applied physics are ilent on most of the processes and devices. The academic and technical physicist will herefore be saved prolonged search if he requires any of the information contained in this ook, and it is unlikely that he will not, in the course of his work, sooner or later have to deal with the materials of which our authors treat.

The metals handled are tungsten, molybdenum, tantalum and niobium; the platinum metals; and a group of other metals, chief among which are nickel, iron and copper, used in vacuum tube construction. There are tables for each separate metal, giving a variety of physical constants, many not usually tabulated. Alloys, mercury and the alkali and alkaline earth metals are then discussed in turn. There follows a special section on the treatment of the metals used in tube construction, dealing, for instance, with welding and soldering. The physical properties of the various glasses used are treated in detail, with full tables, and many other substances, such as mica and asbestos, are discussed in turn. Among other subjects may be mentioned the preparation of phosphorescent screens for cathode ray tubes; the various types of hot cathode; the methods of gettering; and the making of glass-to-metal joints.

The book is full of pieces of useful information. The reader will learn that quartz windows can be sealed to ordinary glass tubes by the use of suitable intermediary glasses: that the use of nickel instead of iron in sealed off tubes is largely due to the insufficient purity of iron, especially carbon contamination; he will find nomograms for obtaining true temperature from the measured "black" temperature of various surfaces, resistance of metal wires and such like; and very compact diagrammatic representation of the purification processes of various gases. The illustrations, some four hundred in number, are strongly to be commended. My only criticism is that the index is very incomplete, which makes the tracing down of particular points a little more troublesome than it need be. The book is one which I shall often open.

E. N. DA C. A.

Handbuch der Experimentalphysik, Band XVI, Teil 1. *Magnetooptik*, by W. Schütz. Pp. x + 378, with 138 figures. (Leipzig: Akademische Verlagsgesellschaft m.b.H.) Price M. 32.

This treatise on magneto-optics, from which the Zeeman effect is excluded, forms a very interesting addition to the Wien-Harms series. It is written in a most engaging style, and the clear legends attached to each figure, the careful dissection and explanation of every mathematical formula, and the precise statement of all symbols in convenient places make the work a particularly valuable book of reference. The data here published have been collected with considerable care and critical discrimination, and they are most adequately discussed.

About half the book is devoted to the theory and experimental technique of the Faraday effect, the rotation of the plane of polarization of light by passage through a medium parallel to the lines of force of a magnetic field. The arrangements of Allison and Beams are, very properly, briefly described and their findings reported. The sections on diamagnetic and paramagnetic rotations are well set forth, but that on ferromagnetic rotation is specially illuminating.

A second portion of the book, some sixty pages, is given to the discussion of magnetic double refraction. The author mentions a very simple method of showing the Voigt effect in which only a small magnet and a spectroscope which will resolve the *D* lines of sodium are required. In connexion with the Cotton-Monton effect some striking data as to the amount of double refraction of nitrobenzene observed with different electromagnets are given, and some little attention is paid to the importance of this effect in the elucidation of problems of the chemical structure of molecules.

The magneto-optics of colloids and large particles are dealt with in a third portion of some fifty pages, and the reflection of light at the surfaces of magnetized bodies in the final portion of about the same length. Throughout the whole treatment the author proves clearly that he has read widely, and that he has not confined his reading to German periodicals. The important theoretical work of C. G. Darwin, for example, is properly appreciated. The whole standard of the work is certainly as high, if not higher than that of the earlier volumes of this Handbuch.

L. F. B.

Dynamics of Rigid Bodies, by William Duncan MacMillan. Pp. xiii + 478. (McGraw-Hill Publishing Company Ltd., 1936.) Price 36*s*.

This is the third volume of a series on theoretical mechanics by Prof. MacMillan of the University of Chicago, the titles of the two previous volumes being "Statics, and the dynamics of a particle" and "The theory of the potential". It is intended to furnish an introduction to the study of rigid dynamics, and to that end it has been made a complete and independent treatment of the subject based firmly upon Newton's laws of motion, and every chapter has been equipped with a fair number of problems. The author states explicitly that the student of rigid dynamics is expected to be well advanced in his mathematical training, and indeed this book does make considerable demands on his knowledge and abilities. The only similar work in English is Whittaker's classical treatise on analytical dynamics, with which the present volume may be justly compared both in its wide scope and in its sound and detailed treatment of the many problems of pure mathematics which arise.

The freshness and originality with which MacMillan discusses the historical problems of dynamics are perhaps best shown by an indication of the many novel features in this work. Vectorial methods are made fundamental throughout. The chapter on systems of free particles includes the permanent configurations in the problem of n attracting bodies. The discussion of motion on a fixed plane includes an elaborate discussion of the friction on a sliding base, allowing for the yielding of the plane. The treatment of the motion of a rigid body about a fixed point includes the integrable case discovered by Mme Kowaleski. The theory of the rolling and spinning of a coin on a horizontal plane is worked out completely in terms of hypergeometric functions. The concluding chapter on the method of periodic solutions gives a rigorous and detailed account of the mathematical theory including some unpublished work of Dr W. Bartky on linear differential equations.

These brief indications will show the great width of the field covered by the author and the diligent care with which it has been intensively cultivated. This work will become a standard treatise on rigid dynamics for the advanced student and lecturer, and Prof. MacMillan has made us all his debtors by the publication of this masterly exposition.

G. T.

The Freedom of Man, by Arthur H. Compton. Pp. xi + 153. (New Haven: Yale University Press; London: Humphrey Milford, Oxford University Press.) Price: 9*s*. net, or $2.00.

In this book the author has brought together the material which was presented as certain foundation lectures in 1931 and 1935. The preparation of these lectures provided him with the incentive to formulate the relationship between his own scientific and religious thinking "much more carefully" than he otherwise would have done. The first lecture is entitled "Freedom versus Law, an Age-long Conflict"; the second lecture on "What Determines Our Actions" contains a very clear exposition of Heisenberg's uncertainty principle in language which can readily be understood by the layman. As a physicist the

hor concludes in this lecture that "there is no reason from the consideration of the
ons of living organisms to doubt the universal validity of the laws of physics; but these
s are insufficient to make possible an exact prediction of such actions". In the third
ure "Intelligence in the World of Nature" the hypothesis is endorsed "of a supreme
elligence working through nature's processes as the only satisfactory method of account-
for the remarkable world in which we find ourselves". The fourth lecture "Man's
ce in God's World" discusses the relation between God and man from a scientist's
nt of view. In the last lecture "Death, or Life Eternal" the author examines the
stion of immortality and concludes "that science finds itself incapable of giving a
inite answer, at present at least". The statement in this lecture (p. 122) "The older
ish teaching has little to say on the question" is open to question. We read for
mple in Psalm xlix "But God will redeem my soul from the grasp of the grave: for he
l receive me" and again in Psalm xvi "For Thou wilt not abandon my soul to the grave;
ther wilt thou suffer thy loving one to see the pit"; and yet again in Ecclesiastes, ch. x,
. "And the dust returneth to the earth as it was, And the spirit returneth unto God who
e it." In addition to these few quotations there are the many ancient Rabbinical
nmentaries on these and similar passages which occur in the Old Testament.

For those with the desire to think beyond their "to-day" the book can be warmly
ommended as an affirmation, in the light of scientific discoveries, of belief in the
damental tenets common to the principal faiths of the world.

H. R. L.

e *Science Masters' Book* (Series II), Parts 1 and 2, by G. H. J. Adlam. Part 1,
pp. xvi+273. Part 2, pp. xvi+252. (London: John Murray.) Price 7*s*. 6*d*. each
part.

I have often thought that it would be amusing to show how very many simple physical
eriments could be performed, qualitatively and quantitatively, with apparatus ordinarily
ilable in every household. By suitable purchases the list of experiments could be
ended very considerably and if the additional apparatus were bought in the cheapest
rkets and instructions for making such simple instruments as the astatic galvanometer,
metre bridge, the monochord etc. were available, an interested student could equip
own private laboratory for an outlay of about a sovereign.

The laws of the simple pendulum can be demonstrated with a plum-bob, or a Newtown
pin. Pins and a convex lens (3*d*.) can be used to illustrate image-formation and to
ke clear the idea of parallax (the golfer should welcome this). A cocoa-tin is a satis-
tory calorimeter. I am reminded of this old idea by the books under review, for in the
ume on physics there are several lists of general apparatus obtainable from toy shops and
res, and here are such instructions as are necessary for their use. Altogether there are
e two hundred notes and experiments, all interesting and some novel, which have been
cted from the *School Science Review*, so that with those included in the first series very
e fields in physics, chemistry and biology are covered in the four volumes.

One of the especial merits of a collection of notes of this kind is that of stimulating the
der to modify, and even, perhaps, to improve upon them. I had not thought of such a
ple way of illustrating Lenz's law as the one described, but only a few minutes were
uired in which to wind two similar coils, one a closed circuit and the other open-ended,
ix them some ten inches apart and to suspend the system from a thread and carry out
demonstration. If, like myself I regret to say, you missed seeing Series 1 (1931) of
se publications, your immediate reaction should be to make amends for the oversight,
these books should be in every laboratory where the above-mentioned sciences are
ht.

J. H. B.

Under the general heading *Actualités Scientifiques et Industrielles* we have receive the monographs listed below. Each is written by an authority on his subject an the treatment is, in general, concise and clear. The publishers are Hermann et Cie 6, Rue de la Sorbonne, Paris.

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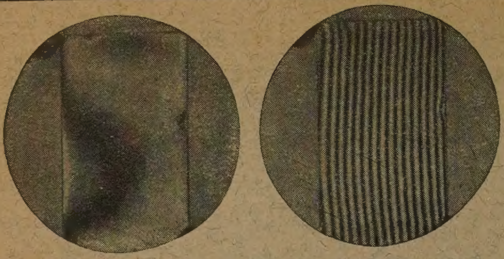

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